(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 878 443 A1

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:
18.11.1998 Bulletin 1998/47

(21) Application number: **97901265.5**

(22) Date of filing: **27.01.1997**

(51) Int. Cl.[6]: **C01B 5/00**

(86) International application number:
PCT/JP97/00188

(87) International publication number:
WO 97/28085 (07.08.1997 Gazette 1997/34)

(84) Designated Contracting States:
CH DE FR GB IT LI NL

(30) Priority: **29.01.1996 JP 12413/96**
12.09.1996 JP 242246/96
06.12.1996 JP 327296/96

(71) Applicants:
- **FUJIKIN Inc.**
  Osaka-shi, Osaka-fu 550 (JP)
- **Hitachi, Ltd.**
  Chiyoda-ku, Tokyo 101 (JP)
- **OHMI, Tadahiro**
  Sendai-shi Miyagi-ken 980 (JP)

(72) Inventors:
- **OHMI, Tadahiro**
  Miyagi 980 (JP)
- **KAWADA, Koji**
  Nishi-ku Osaka-shi Osaka 550 (JP)
- **TANABE, Yoshikazu,**
  Kabushiki-Kaisha Hitachi
  Oume-shii, Tokyo 198 (JP)
- **NITTA, Takahisa,**
  Kabushiki-Kaisha Hitachi
  Oume-shi, Tokyo 198 (JP)
- **IKEDA, Nobukazu**
  Nishi-ku Osaka-shi Osaka 550 (JP)
- **MORIMOTO, Akihiro**
  Nishi-ku Osaka-shi Osaka 550 (JP)
- **HIRAO, Keiji**
  Nishi-ku Osaka-shi Osaka 550 (JP)
- **MOROKOSHI, Hiroshi**
  Nishi-ku Osaka-shi Osaka 550 (JP)
- **MINAMI, Yukio**
  Nishi-ku Osaka-shi Osaka 550 (JP)

(74) Representative:
Crump, Julian Richard John et al
FJ Cleveland,
40-43 Chancery Lane
London WC2A 1JQ (GB)

(54) METHOD FOR GENERATING MOISTURE, REACTOR FOR GENERATING MOISTURE, METHOD FOR CONTROLLING TEMPERATURE OF REACTOR FOR GENERATING MOISTURE, AND METHOD FOR FORMING PLATINUM-COATED CATALYST LAYER

(57) The invention further reduces a size and cost of a reactor for generating water from oxygen and hydrogen, provides high-purity water in an amount necessary for practical use safely, stably and continuously, and allows a platinum-coated catalyst layer formed on an inner wall of a reactor body to maintain high catalytic activity over a long period of time. Specifically, the reactor comprises a body made of a heat-resistant material and having an inlet and an outlet for water/moisture gas, has a gas-diffusing member provided in an internal space of the body, and has a platinum coating on an internal wall surface of the body. Hydrogen and oxygen fed from the inlet is diffused by the gas-diffusing member and then comes into contact with the platinum coating to enhance reactivity, thereby producing water from hydrogen and oxygen. A temperature of the reactor for generating moisture, wherein hydrogen is reacted with oxygen at a high temperature to generate moisture, is held to be below an ignition temperature of hydrogen or a hydrogen-containing gas so that hydrogen is reacted with oxygen while preventing explosive combustion of hydrogen and oxygen. The platinum-coated catalyst layer on the internal wall of the reactor body is formed by treating the surface of the internal wall of the body, cleaning the treated surface, forming a barrier coating of a nonmetallic material of an oxide or nitride on the wall surface, and forming the platinum coating on the barrier coating.

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Description

FIELD OF THE INVENTION

The present invention is primarily used in semiconductor manufacturing facilities. More specifically, the present invention is used for supplying water when silicon dioxide film is affixed by a so-called water oxidation method (or steam oxidation method) using a process chamber.

DESCRIPTION OF THE PRIOR ART

For example, for affixing a silicon oxide film by the water oxidation method in semiconductor manufacture, high-purity water is required.

Consequently, for a conventional affixing of a silicon oxide film, as shown in Fig. 52, a process in which hydrogen gas H_2 and oxygen gas O_2 are allowed to combust in a quartz furnace 50 has been extensively used in which water generated by the combustion of these two gases is fed into semiconductor manufacturing equipment; and the oxide film is formed on the Si wafer surface.

In Fig. 52, numeral 51 designates a hydrogen gas nozzle, 52 a Si chip for ignition held in a vicinity of a top side of the hydrogen gas nozzle 51, and 53 is a heating lamp for heating the Si chip 52. A vicinity at a tip end of the hydrogen gas nozzle 51 inside the quartz furance attains a high temperature from about 1800°C to 2000°C due to flames of combustion. In addition, an amount of oxygen gas O_2 supplied to the quartz furnace 50 is set to a level exceeding one half that of the hydrogen gas H_2 in order to completely combust the hydrogen gas H_2 and to maintain safety, and flow rates of O_2 and H_2 are respectively separately set to several liters/min.

The process of Fig. 52 achieves excellent practical effects in that water thereby generated is of a high purity and can be instantaneously generated at a rate of several liters/min.

However, in the process of Fig. 52, there is a problem in that if the feed rate of hydrogen gas H_2 or oxygen gas O_2 is reduced to decrease the water amount, combustion can easily be thereby stopped and it is therefore extremely difficult to apply controls for decreasing the generated water amount, and a control range of a ratio of water to oxygen (moisture content/oxygen) is narrow.

The process has a difficulty in that because raw gas is fed directly into the reactor pipe, when combustion stops an interlock mechanism becomes indispensable to prevent explosion.

In addition, there is also a problem in that when gas flow rate is reduced, flames are generated in the vicinity of the nozzle, SiO_2 composing the quartz nozzle evaporates, and these volatile materials mix in a reactor atmosphere (H_2O + O_2) and contaminate a gas (H_2O + O_2) fed to the semiconductor manufacturing equipment to such an extent that it can no longer be used for manufacturing high-performance semiconductors.

In the meantime, for solving difficulties of combustion furance type water-generating equipment as shown in Fig. 52, the inventors of this application previously developed a water generating process using the equipment shown in Fig. 53, disclosed in Japanese unexamined Patent Publication No. Hei-6-115903.

That is, this water generating process first mixes hydrogen H_2 , oxygen O_2 and inert gas Ar to form a mixture gas C, the mixture gas C is introduced into a reaction pipe 54 made of a material having a catalytic action that can radicalize hydrogen and oxygen and at the same time the reaction pipe 54 is heated to allow hydrogen and oxygen in the mixture gas C to react, thereby generating water.

The water generating method according to the Japanese Unexamined Patent Publication No. Hei 6-115903 can obtain a mixture gas containing high-purity water ranging from low concentration on a ppb order to high concentration on a percent order, and at the same time is excellent in responsiveness, in ease of maintaining control, and in achieving high effects.

However, the water generating process using the equipment shown in Fig. 53 still has many problems that must be solved.

A first point is that because the mixture gas C of hydrogen and oxygen and argon is introduced into the reaction pipe 54, a reactivity degrades as compared with a case in which only hydrogen and oxygen are supplied, and as a result, the reactor size is increased. In particular, there is a case in which hydrogen or inert gas is added to water to adjust an oxidation-reduction power, and N_2 O, etc. are added to water in order to improve interface characteristics of Si and SiO_2, and in such event, an increase of the reactor size results in an increase of gas consumption rate, posing a serious problem from a standpoint of economy, etc.

It is also a problem that even if hydrogen and oxygen finish the reaction completely, the product gas is a mixture gas of moisture and argon, and it is unable to output high-purity water only or a mixture gas of water and oxygen.

A second problem is a problem of responsiveness and reactivity of water generation. Because stainless pipes are used as a material having the catalytic action and catalytic action of pipe surfaces are utilized, it is unable to achieve a large reaction gas rate per unit surface area.

casing that can activate reactivity of hydrogen or oxygen, and holding an upstream-end temperature of hydrogen and oxygen under reaction in the water-generating reactor at a level lower than a downstream-end temperature in the water-generating reactor by allowing the hydrogen and oxygen to react with each other at a high temperature.

A process for forming a platinum coated catalyst of a water-generating reactor according to this invention comprises cleaning an inner wall surface of a metallic body of a reactor by applying a surface treatment, forming a barrier coating of a nonmetallic material of an oxide or a nitride on the inner wall surface and forming a platinum coated film on the barrier coating in the water-generating reactor, with the platinum coated film formed on the inner wall surface of the metallic reactor body (the body having an inlet and a water and moisture gas outlet) being used as a catalyst, with hydrogen and oxygen supplied through the inlet being brought into contact with the platinum coated film to activate their reactivity and water being generated from the hydrogen and oxygen in the water-generating reactor.

Hydrogen and oxygen, mixed at a ratio of nearly 2:1, are allowed to come into contact with the high-temperature catalyst material surface in the reactor, and radicalized by catalytic action of the catalyst material to directly react and generate water.

The generated water is guided out of an outlet end of the reactor as steam, and thereafter, is mixed with a suitable amount of O_2 , N_2, Ar, etc. and heated, and then supplied to the semiconductor manufacturing equipment.

Because a majority of the reactions between the hydrogen and oxygen take place in a vicinity of the gas inlet end of the reactor, in the first and the second water-generating reactors according to this invention, the inlet end of the reactor is more strongly heated by reaction heat and temperature rises greatly. Consequently, catalytic action at the reaction inlet end is weakened, gas supply position is distributed in a longitudinal direction of the reactor, or an inlet-end heater temperature is lowered so that temperature rise on the reactor inlet end is prevented.

Contrary to this, in the third and fourth water-generating reactors of this invention, because reactions of hydrogen and oxygen take place nearly uniformly throughout whole inside areas of reactor bodies, a temperature of the whole reactor body rises nearly uniformly.

In a water-generating reactor in which a platinum coating catalyst layer is formed according to this invention, the barrier film formed on the inner wall surface of the reactor body prevents metal components forming the reactor body from diffusing into the platinum coated film. Consequently, an amount of metal oxides formed in the platinum coated film greatly decreases and a high catalytic performance of platinum can, thereby, be stably maintained over a long period of time.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a system block diagram showing an embodiment of water-generating equipment using first and the second water-generating reactors of this invention;

Fig. 2 is a schematic cross-sectional view showing a first embodiment of the first water-generating reactor;

Fig. 3 shows a second embodiment of the first water-generating reactor;

Fig. 4 shows a third embodiment of the first water-generating reactor;

Fig. 5 is a schematic cross-sectional view of a gas spouting mechanism of the first water-generating reactor;

Fig. 6 is a cross-sectional view taken on line VI-VI of Fig. 5;

Fig. 7 shows a fourth embodiment of the first water-generating reactor;

Fig. 8 shows a fifth embodiment of the first water-generating reactor;

Fig. 9 shows a sixth embodiment of the first water-generating reactor;

Fig. 10 shows a seventh embodiment of the first water-generating reactor;

Fig. 11 shows an eighth embodiment of the first water-generating reactor;

Fig. 12 shows a ninth embodiment of the first water-generating reactor;

Fig. 13 shows a tenth embodiment of the first water-generating reactor;

Fig. 39 is a plan view of the structure of Fig. 38;

Fig. 40 is a diagram showing temperature of each portion of the reactor according to the first embodiment;

Fig. 41 is a diagram showing changes with passage of time in water generation reactivity in the reactor 1 of the first embodiment;

Fig. 42 is a diagram showing water generating responsiveness of the first embodiment;

Fig. 43 is a schematic longitudinal cross-sectional view showing a second embodiment of the third and the fourth water-generating reactors according to this invention;

Fig. 44 is a schematic longitudinal cross-sectional view showing a third embodiment of the third and fourth water-generating reactors according to this invention;

Fig. 45 is an illustration of water-generating equipment using the third and fourth water-generating reactors;

Fig. 46 shows changes with passage of time in water generation responsiveness in a water-generating reactor having a conventional platinum coated film;

Fig. 47 shows XPS analysis results of a platinum coated film surface after use in a conventional reactor;

Fig. 48 shows XPS analysis results of another platinum coated film surface after use in the conventional reactor;

Fig. 49 shows a longitudinal cross-sectional view of the fourth water-generating reactor according to this invention to which the method for forming the platinum coated catalyst layer of this invention is implemented;

Fig. 50 shows a fragmentary enlarged sectional view of the reactor body of Fig. 49;

Fig. 51 shows changes with passage of time in water-generation-reactivity rate in a water-generating reactor with a platinum coating catalyst layer formed in accordance with this invention;

Fig. 52 is an illustration of known combustion-pipe-type water-generation equipment; and

Fig. 53 is a schematic representation of catalyst-reaction-type water-generating equipment according to an earlier-filed application.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Water Generating Method and First and Second Water-generating reactors and Temperature Control Method

Fig. 1 is a system diagram of water-generating equipment employing a first and a second water-generating reactor. In Fig. 1, reference characters H_2 designates hydrogen gas, O_2 oxygen gas, Ar argon gas for purging, MFC1-MFC4 mass flow controllers, V_1 - V_4 valves, TC1 -TC4 temperature measuring thermocouples, 1 a reactor, 2a - 2d check valves, 3 a heater, 4 an O_2 and H_2 mixing portion, 5 an O_2 and water mixing portion, 5a a heater, and 6 semiconductor manufacturing equipment.

Hydrogen gas H_2 and oxygen gas O_2 supplied to the reactor 1 are set to either 2:1, 3:1 or 4:3 and, as is clear from a test sample 1 later discussed, an H_2-rich mixture gas can lower reaction temperature and water is likely to be generated.

In Fig. 1, a reaction gas is brought to a hydrogen-rich condition, but needless to say, conversely, the reaction gas could also be brought to an oxygen-rich condition.

In Fig. 1, hydrogen and oxygen are to be supplied to the reactor 1 in a gaseous form, but liquefied hydrogen and liquefied oxygen could also be supplied.

Furthermore, in Fig. 1, hydrogen and oxygen are premixed at the mixing portion 4 and supplied to the reactor 1, but it is also possible to supply hydrogen gas and oxygen gas independently to the reactor 1, and to mix them in the reactor 1.

In addition, in Fig. 1, the mixture gas of hydrogen gas and oxygen gas formed at the mixing portion 4 is supplied to the reactor 1 as is, but a preheating section H is provided at an introducing portion of the reactor 1, and the mixture gas

is no fear of gas ignition, that is, gas explosion. In particular, controlling the temperature at the gas inlet end portion of the reactor 1 to be in the vicinity of about 200-500°C, with the reaction heat of the mixture gas taken into account, temperature of each portion of the reactor 1 can be surely held to 600°C or lower, and explosion by ignition can be completely prevented.

At the gas mixing portion 4 of the O_2 gas and the H_2 gas, a regular in-pipe gas mixing system is adopted, and no special gas mixing mechanism at all is used.

Needless to say, a gas mixing mechanism designed to discharge H_2 gas into oxygen gas O_2 in a swirling stream using a mixing box (not illustrated) and to uniformly mix them both, may be used as a gas mixing portion 4.

A gas preheating portion may be installed inside or downstream of the mixing portion 4.

The O_2 and water mixing portion 5 is installed near the outlet end of the reactor 1, and is provided with the heater 5a.

That is, oxygen gas O_2 is mixed with water spouted from the reactor 1, and the mixture gas of H_2O and O_2 is heated to higher than about 120°C by the heater 5a to prevent dew condensation of H_2O on pipe walls, and then supplied to the semiconductor manufacturing equipment 6.

In the reactor 1 of Fig. 1, O_2 is mixed with water, but as a diluting gas, in addition to O_2, H_2 and inert gas for adjusting oxidation-reduction power, or N_2O, etc. for improving interface characteristics of Si and Si O_2 are sometimes used.

In the reactor 1 of Fig. 1, since gases supplied to the reactor 1 are restricted to hydrogen and oxygen only, as compared to a conventional case in which mixture gas (diluting gas) of hydrogen, oxygen, argon, etc. is supplied, the reactivity is improved, and it has an advantage in that the reactor 1 can be downsized a corresponding amount.

Table 1 shows analysis results in which impurities in water generated from the first water-generating reactor 1 according to this invention was analyzed by a flameless atomic absorption analysis.

That is, the generated water was collected by allowing it to condense in the PFA tube, and three components of Cr, Fe, and Ni were analyzed by the flameless atomic absorption analysis. As a result, metals of all three components became low values on the order of ng/mL or less.

TABLE 1

Analysis of impurities in generated water

(flameless atomic absorption analysis)

(Unit: ng/m. liter)

Element	n = 1	n = 2	Mean value
Cr	0.055	0.051	0.053
Fe	1.5	1.6	1.6
Ni	0.69	0.74	0.72

Note) n = 1 and n = 2 indicate the results of measurements carried out twice.

TABLE 2

	Chemical component (wt %)						
	Ni	Cu	Fe	Mn	C	Si	S
Min.	99.0	-	-	-	-	-	-

Needless to say, a heater (illustration omitted) is installed to each of the reactor units 8a, 8b, 8c, respectively.

Fig. 8 shows a fifth embodiment of the reactor 1, where a number and length of catalyst pipes 1b are varied to lower a reactivity at a mixture gas inlet end and to increase outlet end reactivity, with a distribution of reaction heat being designed to be uniform in the longitudinal direction of the reactor 1.

In Fig. 8, the heater is omitted.

Sixth Embodiment

Fig. 9 shows a sixth embodiment of the reactor 1, where an H_2 and O_2 mixture gas inlet end and water outlet end are designed to be placed at the same end, with the inlet end being cooled by the generated water to prevent the inlet end from being heated to high temperature.

Fig. 10 shows a seventh embodiment of the reactor.

In this embodiment, a plurality of branch pipes 9a, 9b, 9c are mounted on a catalyst pipe 1b or a casing 1a. O_2 gas (for example, 500/cc/min.) and part of H_2 gas (for example, 250 cc/min.) are supplied from an inlet end of the catalyst pipe 1b (or casing 1a), and a remainder of H_2 (for example, 250 cc/min.) is supplied from each of branch pipes 9a, 9b, 9c.

By distributing the position of the H_2 gas supplied in this way, it is intended to prevent an overheating caused by reaction heat at the inlet end of the catalyst pipe 1b (or casing 1a).

Eight Embodiment

Fig. 11 shows an eighth embodiment of the reactor 1, in which a catalyst assembly 7 of the reactor 1 is formed to have a plurality of catalyst pipes 1b in parallel, while at the same time an inlet end of each catalyst pipe is positioned to be separated and dispersed from the inlet ends of the other catalyst pipes.

The mixture gas is fed at a flow rate of, for example, 200 cc/min. for O_2 and 400 cc/min. for H_2 from the inlet of the catalyst pipe $1b_1$, and 200 cc/min. for O_2 and 100 cc/min. for H_2 from the inlet of each catalyst pipe $1b_2$, $1b_3$, $1b_4$.

With this configuration, the generation of reaction heat is dispersed and temperature control of the reactor 1 is facilitated.

Ninth Embodiment

Fig. 12 shows a ninth embodiment of the reactor 1, in which two (or more) catalyst pipes $1b_1$, $1b_2$ are installed in parallel and at the same time, the mixture gas is supplied into each catalyst pipe $1b_1$, $1b_2$, respectively, from opposite directions.

In this embodiment, reaction heat at the inlet end is utilized for promoting reaction of the mixture gas at the outlet end, thereby saving energy and at the same time preventing overheating of the catalyst pipe at the inlet end.

Tenth Embodiment

Fig. 13 shows a tenth embodiment of the reactor 1, in which a heat medium gas such as N_2, Ar, CO_2, etc. is allowed to flow between the casing 1a and a nickel tube 1b to transfer reaction heat at an inlet end to an outlet end, and reaction heat thus transferred is utilized to promote reactions at the outlet end.

A heater 3 may be wound around the outside of the nickel tube 1b (catalyst pipe 1b).

Fig. 14 shows a system diagram of experimental equipment used for obtaining basic data required for creation of this invention.

In Fig. 14, MFC1-4 designate mass flow controllers, RP a vacuum pump, and T a tank. As a reactor 1, a nickel pipe (inner surface area 273 cm^2) 1/4 inch inside diameter and 2 m long is used.

Test Example 1

The relationship between the H_2, and O_2, mixture ratio and reaction temperature was tested using the experimental equipment of Fig. 14.

As is clear from Figs. 15 through 18, an H_2 rich mixture gas is likely to lower reaction temperature and generate water easily.

In addition, as is clear from Fig. 19, in the case of the reactor of this test equipment, when the mixture-gas-flow rate became 75 cc/min. or more at 500°C, unreacted O_2, increases.

The curve A shows H_2O, curve B H_2, and curve C O_2, respectively.

inlet end of the reactor is held to 200-500°C and the gas temperature in the vicinity of the outlet end to about 600°C or lower, there is no fear of causing explosion, etc., while a required amount of high-purity water can be generated with high responsiveness.

Third and Fourth Water-generating reactors

Fig. 34 through Fig. 45 show other embodiments of the third and the fourth water-generating reactors.

As a metal catalyst material that can activate the hydrogen or oxygen reactivity, platinum, nickel, stainless steel, etc. exist, and of all these, platinum provides excellent catalyst.

However, platinum is expensive and has a problem from the viewpoint of economy. In particular, when the reactor pipe in the reactor shown in Fig. 2 or Fig. 3 is made of platinum, there is the problem that the manufacturing cost of the reactor soars.

Consequently in the reactor of Figs. 2 or 3, the reactor pipe is made of nickel or stainless steel, or a method of using a platinum-plated nickel or stainless steel pipe as the reactor pipe is adopted, but when the nickel pipe and stainless steel pipe are used as the reactor pipe, the water generation amount per unit surface area of the reactor pipe is small, and there is a problem in that the size of the reactor must be significantly increased in order to produce water of about 1 L/min. or more.

For example, it has been demonstrated that when reactor piping comprising a parallel combination of 1/4" x 280 mm x 19 pieces of nickel piping (nickel surface area: about 1800 cm^2, reactor pipe inner volume: about 300 cm^3, 2 pieces of 1/4" straight pipe about 13m long connected in series) (1/4" straight pipe about 26m long) is used to allow 100 cc/min. of H_2 and 56 cc/min. of O_2 to flow at 500°C, an upper limit of the usable water generation rate is about 100 cc/min. (Max.).

However, since in actual semiconductor manufacturing equipment, a water generation rate exceeding 1 liter/ min. is generally required, a significantly large-size reactor is required to secure the required water generation rate.

When nickel pipe is used as the reaction pipe, a problem of oxide corrosion on the reaction pipe outer surface arises.

For example, when 50 cc/min. of H_2 and 27.5 cc/min. of O_2 are supplied to 1/4" x 200 mm nickel reactor pipe and water is generated for 5 hours at 500°C, it has been confirmed by SEM analysis that about 90% reactivity of water generation reaction can be obtained, but oxide scale about 0.5μm thick is formed on the outer surface of the nickel reactor pipe.

On the other hand, when the temperature of the nickel reactor pipe is lowered to 350°C, formation of oxide scale on the reactor tube outer surface is reduced to a nearly negligible level, but reactivity of the water generation reaction conversely lowers from about 90% to 50-60%, and as a result, the water generation amount markedly decreases.

In this way, when nickel pipe is used as the reactor pipe, the upper limit of the reaction temperature is restricted to about 350°C from a viewpoint of oxide scale generation, and, as a result, the reactor size must still be increased due to the decrease in water generation amount.

It has been confirmed that even if oxide scale forms on the nickel reactor pipe surface, the water generation ratio increases as temperature rises. However, when oxide scale is generated on the reactor pipe surface, contamination of the generated water results, and consequently, the reaction temperature of the reactor pipe must be held to about 350°C or lower (Max.) as described before.

As described above, in order to permit an increase of the generated water volume while downsizing the water-generating reactor, it is essential to use platinum whose catalytic activity at low temperature is significantly higher than that of nickel, etc. as a catalyst in the form of a coating or plating layer.

Therefore, to investigate platinum catalytic activity in more detail, reactor pipes as shown in Figs. 34 and 35 were fabricated and water generating tests were carried out.

That is, in Figs. 34 and 35, reference character E designates a Hastelloy pipe (1/4", 200 mm in total length), H designates a heater, T designates thermometers, Pt a platinum foil catalyst (thickness: 0.05 mm; width: 5 mm; length: 100 mm), and platinum surface area 10 cm^2.

From the gas inlet end of the reactor pipe, H_2, O_2 and N_2 gases are allowed to flow at ratios shown in Table 3, and a reactivity at the reactor pipe outlet, as well as temperatures of the gas at the upstream end, T_1, and the downstream end, T_2, were measured, respectively.

In Table 3, numeral *1 designates the value just after the gas is passed and *2 designates the value obtained when temperature has risen by self heat generation after the gas is passed and reaction is stabilized.

TABLE 4

Material	Gas flow rate (cc/min.)			Heater	Temperature (°C)		Reactivity (%)
	H_2	O_2	N_2		Upstream end	Downstream end	
Pt coated on Ni thin sheet (10 cm^2) Thickness (300 - 400Å) (t 0.1 xw5 xL50 mm x2)	25	25	100	*2 OFF	123	63	98.7
				ON	137	100	99.5
				ON	150	150	99.7
				ON	200	200	100
	25	25	100	*2 OFF	138	65	99.2
				ON	152	100	99.2
				ON	165	150	99.5
				ON	200	200	100
	50	50	200	*1 OFF	29	30	5.5
				*2 OFF	208	130	98.0
				*3 OFF	190	174	98.0
				*4 OFF	35	38	0

The results of the test confirmed that 1) even with a Ni thin sheet having a platinum coating, high catalytic activity of a level similar to that of platinum foil can be obtained, 2) even under O_2-rich condition, nearly 100% reactivity can be achieved, 3) when no diluting gas is present, even at room temperature, the mixture gas ($H_2 + O_2$) is ignited, 4) due to rapid temperature rise, the Ni thin sheet having the Pt coating suddenly loses the catalytic activity, etc.

By analyzing the surface of the Pt coating film on the Ni thin sheet after catalytic activity is lost, causes of the sudden loss of catalytic activity of the N1 thin sheet with the Pt coating have been confirmed to be due to a temperature rise of the Ni thin sheet caused by reaction heat causing substrate metal (Ni) to diffuse into the Pt coating film, and this is oxidized in the Pt coating film by the oxidizing environment. As a result, when the platinum coating film is formed on the surface of the Ni thin sheet, as described above, there is a possibility of losing the catalytic activity, and therefore, the problem of its stability as a reactor remains.

First Embodiment of Third and Fourth Reactors

Referring again to the drawings, a first embodiment of the third and fourth water-generating reactors according to this invention will be described.

Fig. 38 and Fig. 39 show the first embodiment of the third and the fourth water-generating reactors, and correspond to a 11th embodiment reactor, overall. In Figs. 38 and 39, numeral 10 designates a reactor, numeral 11a a reactor body, numerals 12, 13 reactor-body members (flanges), numeral 14 platinum coating film, numeral 15 an inlet for raw material gas, numeral 16 a water and moisture gas outlet, numeral 17 a gasket, numeral 18 a clamp, numeral 19 a heater, and numeral 20 thermocouples.

The reactor 10 comprises two reactor body members (flanges) 12, 13 installed opposite to each other via the gasket 17 and air-tightly tightened and fixed by the clamp 18 with a specified space maintained between them. The reactor

TABLE 5 (continued)

Test No.	H_2 cc/min.	O_2 cc/min.	Temperature (°C)			Time (min.)	Reactivity (%)
			Set	(3)	(4)		
4	50	50	120	113	124	30	98.03
5	480	480	120	200	355	120	99.55
6	50	50	120	113	124	30	95.24
7	50	50	200	-	-	30	98.67
8	50	50	250	-	-	30	99.32
9	50	50	120	-	-	30	94.92
10	480	480	120	201	354	120	99.27
11	50	50	120	113	124	30	93.91
12	480	480	120	200	353	120	99.15
13	50	50	120	113	124	30	94.15
14	480	480	120	202	354	600	99.30
15	50	50	120	-	-	30	94.10

Table 5 shows test conditions of test example 6 using a reactor according to the above-mentioned first embodiment and the test results thereof.

Fig. 40 shows temperature change of each temperature measuring portion in Test No. 1, Test No. 2, and Test No. 3 of Table 5.

That is, reference characters a, b, c show temperature changes of three thermocouples 20a, 20b, 20c mounted on the reactor body member (flange) 12 (without platinum coating film), and the results of No. 1 test are shown with a_1, b_1, c_1, the results of No. 2 test are shown with a_2, b_2, c_2, and the results of No. 3 test are shown with a_3, b_3, c_3, respectively.

The reference characters d, e, f show temperature changes of three thermocouples mounted on the reactor body member (flange) 13 (with platinum coating film), and d_1, e_1, f_1, show the results of No. 1 test, d_2, e_2, f_2, the results of No. 2 test, and d_3, e_3, f_3, the results of No. 3, respectively.

In addition, references character g shows temperature of the downstream-end piping of the reactor 10 and reference character h shows the gas temperature at the H_2 and O_2 mixing portion, and test results indicate that these two temperatures g, h scarcely change in any of No. 1 test, No. 2 test, and No. 3 test.

As is clear from Fig. 40, in No. 1 test (H_2: 50 cc/min.; O_2: 50 cc/min., reactor temperature adjusted at 120°C) of Table 5, temperature d_1 of the gas inlet end portion of the reactor body member (flange) 12 provided with the Pt coating film 4 rose by about 10°C due to the reaction heat generated, and the reactivity was 99.55%.

In No. 2 test (test was started with H_2: 250 cc/min.; O_2: 250 cc/min., and reactor temperature adjusted at 120°C and the heater 9 was turned off midway), temperature d_2 of the gas inlet end portion of the reactor body member (flange) 13 rose by about 100°C and at the same time, temperature of the other portions exceeded the initial adjusted temperature of 120°C due to reaction heat generated, and the reactivity was 99.75%.

In addition, in No. 3 test (test was started with H_2: 480 cc/min.; O_2: 480 cc/min., and reactor temperature adjusted at 120°C and the heater 19 was turned off midway), temperature at the gas inlet end portion of the reactor main member (flange) 13 exceeded 350°C and the reactivity was 99.58%.

However, in all of No. 1 test to No. 3 test, gas temperature h at the H_2 and O_2 mixing portion was held at room temperature, suggesting that H_2 and O_2 are not reacted by ignition.

Fig. 41 shows a relationship between passage of time and reactivity as observed when the reactor 10 is used over a long period of time, and curve C shows the reactivity as observed when the reactor is used with H_2: 480 cc/min.; and O_2: 480 cc/min.

It indicates that when the reactor is used with H_2: 480 cc/min.; O_2: 480 cc/min., a lowering of reactivity is scarcely observed even after operation for 18 hours.

Fig. 42 shows a relationship between passage of time and water generation reactivity as observed when the reactor is used with the reactor temperature held to about 400°C and the reactor has operated as long as 100 hours, and the curve A shows the case of H_2:O_2 = 1000 cc/min.: 1000 cc/min., the curve B the case of H_2:O_2 = 1000 cc/min.: 500 cc/min., and the curve C the case of H_2:O_2 = 1500 cc/min.: 500 cc/min., respectively.

As is clear from Fig. 42, even if the material gas is so-called oxygen rich gas ($H_2/O_2 < ½$), or hydrogen rich gas

which corresponds to a 13th embodiment of the water-generating reactor. In Fig. 44, a conical filter 35 is inserted into a reactor body member 34a forming a reactor 33, and at the same time, a platinum coating film 36 is formed over nearly a whole area of an inner surface of the reactor body member 34a.

With the reactor 33 depicted in Fig. 44, it has been verified that, as with the embodiment of Fig. 43, a specified amount (about 1 liter/min. or more) of water can be stably generated under high reactivity and responsiveness conditions without causing local overheating of the platinum coating film 36.

Regarding the filter 35 of Fig. 44, by making a center bottom portion thereof, opposite a water and moisture gas outlet, to be a non-gas penetrating portion, it is possible to further reduce an amount of unreacted gas and an improvement of water generation reactivity is possible.

Fig. 45 shows a system outline of water-generating equipment using the third and fourth water-generating reactors according to this invention. In Fig. 45, H_2 designates hydrogen gas, O_2 oxygen gas, N_2 nitrogen gas for purge, MFC1-MFC5 mass flow controllers, V_1 - V_5 valves, TC1 - TC6 temperature measuring thermocouples, CV_1 - CV_5 check valves, F_1 - F_3 filters, 37a, 37b gas preheating coils, 38 an O_2 and H_2 mixing portion, 39 an O_2 and water mixing portion, and 40 a semiconductor manufacturing equipment.

Hydrogen gas H_2 and oxygen gas O_2 supplied to the reactor 33 are set to either 2:1 or 2:2, and, in general, an O_2-rich mixture gas is supplied to the reactor 13.

An O_2 and H_2 supply gas pressure is selected to be about 1.1 - 1.05 kg/cm^2 with a flow rate of O_2 = about 1000 cc/min., H_2 = about 1000 cc/min., respectively, and with 1000 cc/min. of water being generated.

The gas preheating coils 37a, 37b are installed to heat the mixture gas or O_2 gas to an optional temperature of about 200°C or lower, but when the mixture gas is room temperature, the gas preheating coil 37a is in general set in a nonoperating state.

The reactor 33 is equipped with a heater and, where necessary, cooling equipment, during operation of the reactor 33, the temperature being controlled to not allow reaction heat to heat the reactor 33 to over 500°C by adjusting the supply rates (water generation rate) of O_2 and H_2 or by operating the cooling equipment.

In addition, a temperature of an oxygen and water mixture in the oxygen (O_2) and water mixing portion 39 mounted in a vicinity of an outlet end of the reactor 33, is maintained constantly at about 120°C to prevent dew condensation of H_2O on a pipe wall, and a heater is equipped as is required.

In this water-generating equipment, the reaction gas is brought to the oxygen rich condition, but, as shown in the curve C of Fig. 42, needless to say, it may be a reaction gas in a hydrogen-rich condition. For example, when forming a silicon oxide film ($SI0_2$) or other films, reducing gas can produce higher quality film.

In Fig. 45, hydrogen and oxygen are to be supplied to the reactor 33 in gaseous form, but liquefied hydrogen and liquefied oxygen may be supplied instead.

Furthermore, in the water-generating equipment of Fig. 45, hydrogen and oxygen are premixed at the mixing portion 38 and then supplied to the reactor 33, but hydrogen gas and oxygen gas may be independently supplied the reactor 33, and mixed in the reactor 33.

In addition, in the water-generating equipment, O_2 is mixed with moisture. But, in addition to O_2, H_2 or an inert gas may be used as a diluting gas for adjusting oxidation and reduction power, or N_2O may be used for improving interface characteristics of Si and $Si0_2$.

Using the water-generating equipment of Fig. 45, gas consisting of 1000 cc/min. of O_2 and 1000 cc/min. of H_2 were supplied and 1000 cc/min. water was continuously generated for about 20 hours, and at the same time, impurity of the generated water and deterioration of the Pt coating film of the reactor were investigated.

The impurity in the generated water was analyzed by a flameless atomic absorption analysis, but the impurity components were all in an order of ng/m liter or less, and no impurity component that would cause a problem was detected.

The Pt coated film was inspected by SEM observation, and there were partly discolored portions but peeling off of the Pt coating film or excessive change in quality caused by oxidation, etc. was hardly observed.

In addition, it has been proven that reactivity tends to be slightly lowered with passage of time as shown in Fig. 41, but since it is maintained at a value higher than about 95%, a practical amount of water generation can be obtained even in O_2 rich conditions.

In the third and the fourth water-generating reactors of this invention, the platinum coating films are formed on surfaces of inner walls of reactor bodies forming the reactors for contacting and activating the O_2 and H_2 gas.

As a result, a platinum consumption rate decreases as compared that of a conventional reactor using platinum foil, platinum pipe or nickel pipe with platinum plating as the catalyst material. Also, construction of the reactors themselves can be simplified, manufacturing costs can be reduced, and, at the same time, the reactor bodies can be greatly downsized, as compared to conventional reactors which use nickel, etc. as the reaction material.

In addition, because a gas diffusing device is installed inside each reactor body, the platinum coating film, the catalyst material, is not locally heated.

As a result, peeling of the platinum coating film, or surface degradation due to oxidation, etc., can be effectively prevented while stable water generation can be continuously carried out under high reactivity and high responsiveness

external surface of sample B, respectively.

In Fig. 47 and Fig. 48, the abscissa is expressed in etching time, with 1 minute of etching time corresponding to a film thickness of about 60-70Å.

As is clear from Fig. 48, in the case of sample B, Fe and O exist in large amounts in the surface layer portion of the coating film on the stainless steel surface after it is used for 3 hours, and the existing amount of Pt is extremely small (about 5%). That is, it is indicated that since the external surface layer portion of the coating film is occupied by iron oxides such as FeO, etc., and the Pt component is decreased, the lowering of the reaction rate results.

Similarly, as clear from Fig. 47, in the case of sample A, it is suggested that the surface layer portion of the coating film on the stainless steel inner surface after it is used for 3 hours is occupied by Ni and O, and the Pt component is nearly zero.

That is, the results displayed in Fig. 47 and Fig. 48 indicate that because of the temperature rise of the substrate stainless steel or Ni film caused by the reaction heat when water is generated, Ni or Fe is diffused in the platinum coating film from the substrate metal, and this is oxidized in the platinum coating film by the oxidizing environment, which is a main cause of loss of catalytic activity of the platinum coating film.

The test results of Fig. 47 and Fig. 48 indicate that a material which does not contain any Ni or Fe component and which does not generate oxides in the platinum coating film is best suited as a substrate film (barrier film) to be formed on the stainless steel surface.

Therefore, the inventors of this invention have reached the conclusion that the high catalytic activity of platinum coating film can be maintained over a long period of time even at a high temperature by using a film which superbly functions to prevent metal diffusion caused by heat as a barrier film intermediately installed between the stainless steel and the platinum coating film.

Based on the above-mentioned conclusion, the inventors of this invention have formed platinum coating catalysis layer as combinations of barrier films of various materials and platinum coating films on inner surfaces of stainless-steel wate-generating reactors, and at the same time, have carried out water generating tests using each platinum coating catalyst layer and investigated changes of the water generation reaction rates (catalytic activity) occurring with time.

This invention of a process of forming platinum coating catalysis layers of water-generating reactors is based on the above-mentioned investigation results.

Embodiments of the Process for Forming Platinum Coating Catalytic Layers

Fig. 49 shows a vertical, sectional view of a water-generating reactor for practicing the process of forming the platinum coating catalysis layer of this invention, and in Fig. 49, numeral 21 designates a reactor, numerals 22, 23 reactor bodies, numeral 24 a gas supply joint, numeral 25 a joint for removing water and moisture gas, numeral 26 a filter flange, numeral 27 a reactor fixing bolt, numeral 28 a gas diffusing member, numerals 29a, 29a' reflector plates, numeral 30 a filter, numeral 31 a filter retainer, and numeral 41 a platinum coating catalyst layer. The reactor 21 is formed in a short cylindrical shape by air-tightly linking two stainless steel (SUS316L) reactor bodies 22, 23.

Because the structure of the water-generating reactor of Fig. 49 is identical to the fourth water-generating reactor of this invention described in conjunction with Fig. 43, a detailed explanation will be omitted.

In the water-generating reactor of Fig. 49, the platinum coating catalyst layer 41 is formed on the entire inner surface of the reactor body 23 made of SUS316L and, as shown in Fig. 50, after a TiN barrier film 42 is formed on the inner surface of the reactor body 23, a platinum coating film 43 is formed on the barrier film 42. The platinum coating catalyst layer 41 according to this invention is formed of the barrier film 42 and the platinum coating film 43.

A thickness of the platinum coating film 43 is preferably from 0.1 μm to 3 μm, and, in this embodiment, the platinum coating film 43 is formed to be about 1 μm thick.

A thickness of the barrier film 42 is preferably from 0.1 μm to 5 μm, and in Fig. 50, the TiN barrier film 42 is about 2 μm thick.

Specific Example of Process for Forming Platinum Coating Catalyst Layer

In forming the platinum coating catalyst layer 41, the recessed inner surface of the reactor body 23 formed in a specified shape is properly surface-treated and various metal oxide films and passive-state films naturally formed on a stainless steel surface are removed. Any method may be used for this surface treatment.

When the surface treatment of the inner surface of the recess 23a is completed, the barrier film 42 of TiN is formed. In this embodiment, a TiN barrier film 42 about 2 μm thick is formed by an ion plating method.

For this barrier film 42, TiC, TiCN, TiAlN, etc. may be used in addition to TiN.

The thickness of the barrier film 42 is suitably from 0.1 μm to 5 μm as described above. This is because if the thickness is less than 0.1 μm, the barrier functions are unable to be satisfactorily carried out, and, on the contrary, if the thickness exceeds 5 μm, it takes undue time to form the barrier film 42 itself. Even if the thickness is more than 5 μm, its

ried out at 400°C for a total of 10 hours using the water-generating reactor of Fig. 49, to which this invention was applied (the one used for the measurement of curve A of Fig. 51).

TABLE 6

Element	Fe	Cr	Ni	Pt
Detection concentration (ng/mL= ppb)	0.17	0.037	<0.05	<0.01
Detection limit of the detector (ppb)	0.02	0.02	0.05	0.01

An analysis of above trace elements was conducted by a graphite reactor heating-atomic absorption analysis process (polarization Zeeman atomic absorption photometer available from Hitachi) for Fe, Cr and Ni, and by an ICP mass spectrometry (ICP mass spectrometer available from Seiko Denshi) for Pt.

As is clear from Table 6, trace elements in the generated water are all extremely insignificant. It is clear that Pt is scarcely dissolved into water from the platinum coating film 43, because Pt existing in the measuring system is only the portion of the platinum coating film 43.

In the process for forming the platinum coating catalyst layer of this invention, after the inner wall surface of the water-generating reactor is cleaned, the barrier film of TiN, etc. is formed on it, and thereafter the platinum coating film is formed on the barrier film.

As a result, even when the reactor body is heated to a high temperature of about 400°C., diffusion of metal components of the substrate forming the reactor body into the platinum coating film can be almost completely prevented by the barrier film of TiN, etc., and the rate of formation of metal oxides in the platinum coating film can be greatly reduced, and the high catalytic performance of Pt is able to be stably maintained over a long period of time.

It is possible to economically form the platinum coating catalyst layer 41 in high efficiency and with a minimum amount of platinum on the surface of the stainless steel reactor body, and at the same time it is possible to maintain the water generation reaction rate of the reactor at a nearly constant level over a long period of time while, at the same time, the generated water is not contaminated with dissolution of Pt.

Claims

1. A process for generating water from hydrogen and oxygen in which hydrogen and oxygen are supplied into a reactor equipped with a material having catalytic action to activate a reactivity of hydrogen and/or oxygen and the reactor temperature is maintained below an ignition temperature of hydrogen and gas containing hydrogen to allow hydrogen and oxygen to react and generate water while preventing combustion of hydrogen and oxygen.

2. The process for generating water of claim 1 wherein hydrogen and oxygen are allowed to react while temperature at a vicinity of a hydrogen and oxygen inlet end of the reactor is held to 200°C to 500°C and temperature in a vicinity of a water outlet end of the reactor is held to about 600°C or lower.

3. The process for generating water of claim 1 wherein a supply ratio of a volume of hydrogen gas to that of oxygen is set to 1:not less than 0.5 or 1:not higher than 0.5.

4. The process for generating water of claim 1, claim 2, or claim 3 wherein the water generated in the vicinity of an outlet end of the reactor is diluted and gas containing water of an optional concentration is guided out.

5. A water-generating reactor in which cylinders made of a material having catalytic action that can activate a reactivity of hydrogen and/or oxygen or a material whose surface is covered with the material having the said catalytic action are placed in a casing to form passages through which hydrogen and oxygen flows while making contact with inner wall surfaces and/or outer wall surfaces of the cylinders, and a heater is placed outside or inside of the casing.

6. The water-generating reactor of claim 5 wherein hydrogen and oxygen are introduced into the inside of at least one of the cylinders and guided therein to flow towards the outlet end, then guided outside the cylinder to return to flow towards the inlet end, and is thereafter introduced into the inside of another cylinder from the inlet end and guided therein to flow towards the outlet end.

7. The water-generating reactor of claim 5 or claim 6 wherein the cylinder is a pipe made of nickel.

gen H_2/O_2 is $H_2/O_2 > ½$.

20. The water-generating reactor of claim 16 wherein the gas diffusing member comprises a reflector plate located opposite the inlet and a filter located downstream of the reflector plate or a reflector plate located opposite the inlet, a filter located downstream of the reflector plate, and a reflector plate located opposite the water and moisture gas outlet.

21. The water-generating reactor of claim 16 wherein the gas diffusing member comprises a cylinder, cone, or disk made of a filter placed opposite the inlet.

22. The water-generating reactor of claim 16 wherein the gas diffusing member comprises a disk placed opposite the inlet and having a filter at a periphery portion.

23. The water-generating reactor of claim 18 wherein the barrier film is made of at least one of TiN, TiC, TiCN, or TiAlN.

24. A process for controlling temperature of a water-generating reactor which has a catalyst in a casing that can activate reactivity of hydrogen or oxygen and in which hydrogen and oxygen are allowed to react with each other to generate water at high temperatures, wherein an upstream-end temperature of hydrogen and oxygen under reaction in the said water-generating reactor is held lower than that of a downstream-end temperature.

25. The process for controlling temperature of the water-generating reactor of claim 24 wherein the upstream-end temperature of hydrogen and oxygen under reaction is held in a range of from 200°C to 500°C and the downstream-end temperature is held at about 600°C or lower.

26. A process for controlling temperature of a water-generating reactor which has a catalyst in a casing that can activate a reactivity of hydrogen or oxygen and in which hydrogen and oxygen are allowed to react at high temperatures to generate water, wherein areas of contact between the catalyst in the casing and a mixture gas are smaller on upstream-end reacting gases than on a downstream-end reacting gases to reduce reaction amounts of oxygen and hydrogen so that a temperature rise at the upstream-end reacting gas is prevented..

27. A process for controlling temperature of a water-generating reactor which has a catalyst in a casing that can activate reactivity of hydrogen and/or oxygen and in which hydrogen and oxygen are allowed to react at high temperatures to generate water, wherein a catalytic action of the catalyst in the casing is designed to be smaller on upstream-end reacting gases than on downstream-end reacting gases to reduce reaction amounts of oxygen and hydrogen so that a temperature rise on the upstream-end reaction gases in the casing is prevented.

28. A process for controlling temperature of a water-generating reactor which has a catalyst in a casing that can activate reactivity of hydrogen and/or oxygen and in which hydrogen and oxygen are allowed to react at high temperatures to generate water, wherein positions for supplying gases to come in contact with the catalyst in the casing are scattered to reduce reaction amounts of oxygen and hydrogen at the upstream end so that temperature rises of upstream-end reacting gas in the casing is prevented.

29. A process for forming a platinum coated catalyst layer in a water-generating reactor in which a platinum coated film formed on an inner wall surface of a metal reactor body having an inlet as well as a water and moisture gas outlet serves as a catalyst for activating a reactivity of hydrogen and oxygen supplied from the inlet, with the oxygen and hydrogen being brought into contact with the platinum coating film to generate water from the hydrogen and oxygen in the reactor, wherein the inner wall surface of the said metal reactor body is surface-treated by cleaning, then a barrier film of nonmetallic material of oxides or nitrides is formed on the inner wall surface of the reactor body, and thereafter the platinum coated film is formed on the barrier film.

30. The process for forming the platinum coated catalyst layer in the water-generating reactor of claim 29 wherein the barrier film is made of one of TiN, TiC, TiCN, TiAlN, Al_2O_3, Cr_2O_3, SiO_2, and CrN.

31. The process for forming the platinum coated catalyst layer in the water-generating reactor of claim 29 wherein the reactor body is made of stainless steel and the barrier film is a film made of TiN.

32. The process for forming the platinum coated catalyst layer in the water-generating reactor of claim 29, claim 30, or claim 31 wherein the thickness of the barrier film is 0.1 - 5 μm and the barrier film is formed by an ion plating method

FIG. 1

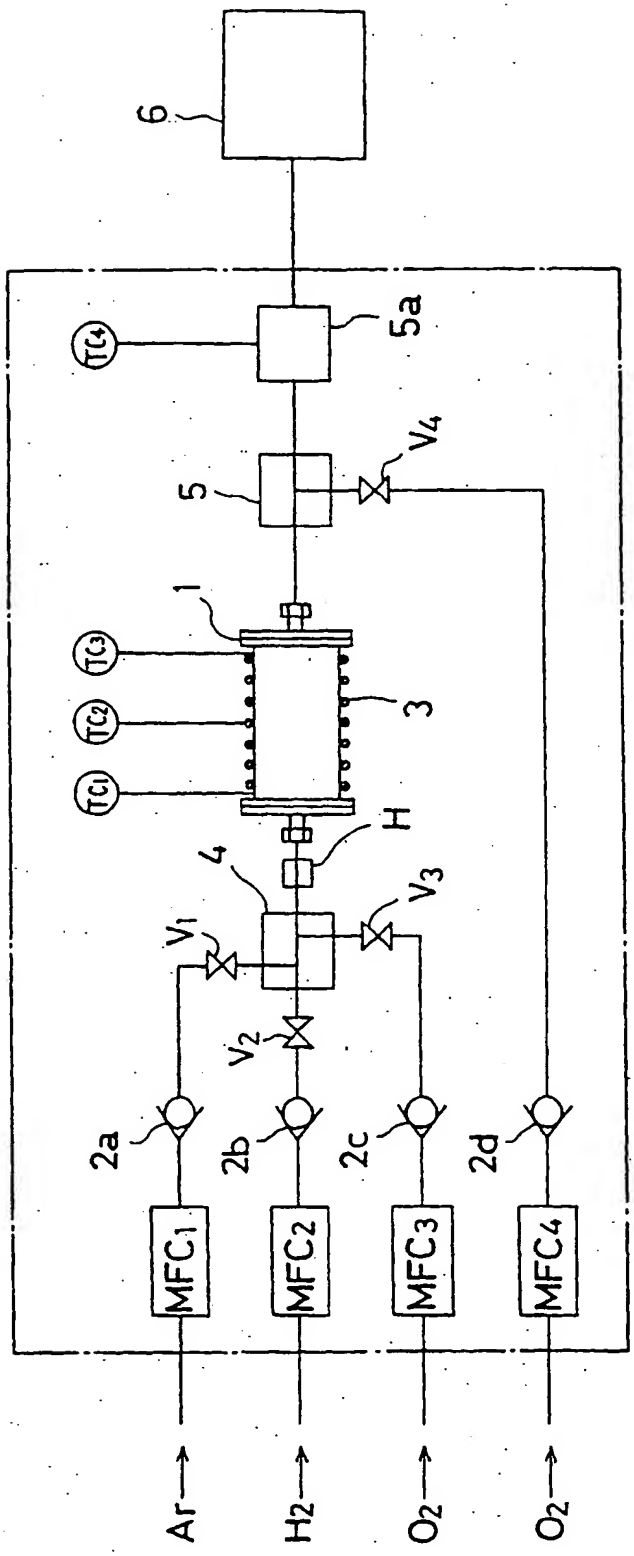

6
5a
TC4
5
V4
1
TC3
TC2
TC1
3
H
4
V3
V1
V2
2a
2b
2c
2d
MFC1
MFC2
MFC3
MFC4
Ar
H2
O2
O2

FIG. 4

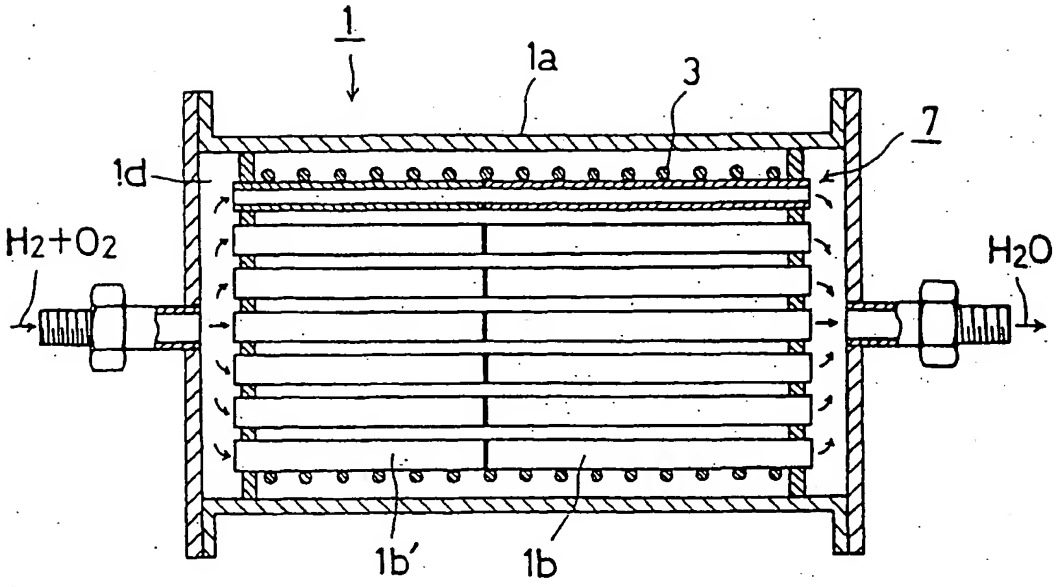


FIG. 5

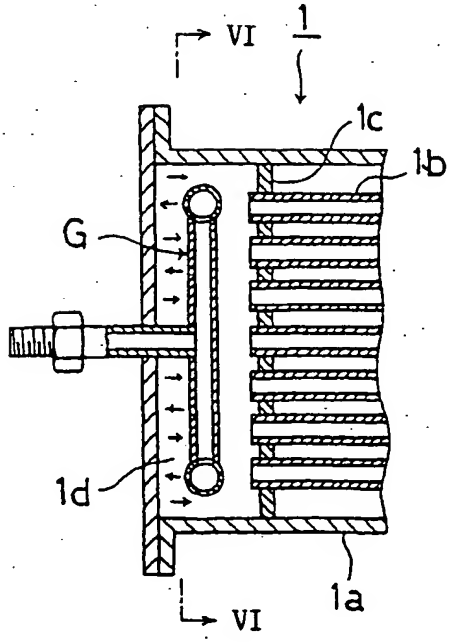


FIG. 9

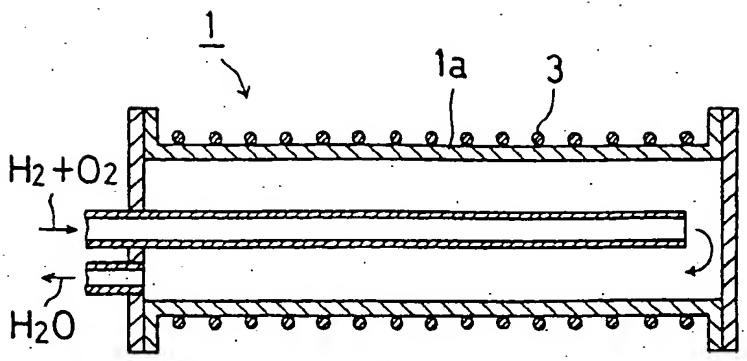


FIG. 10

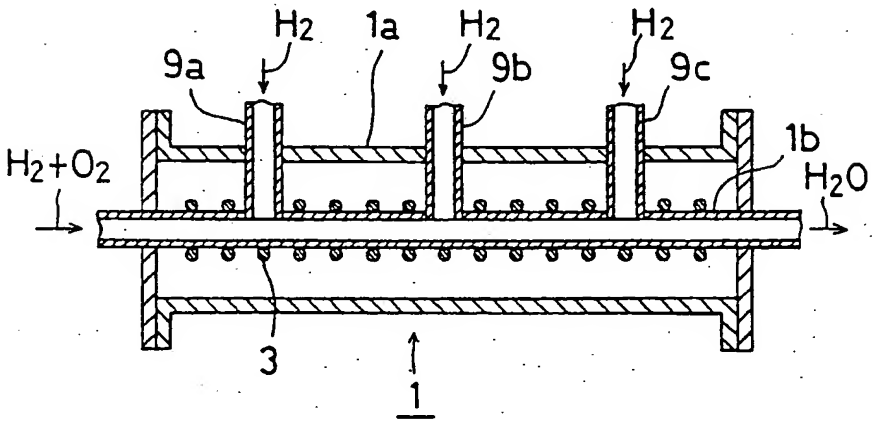


FIG. 11

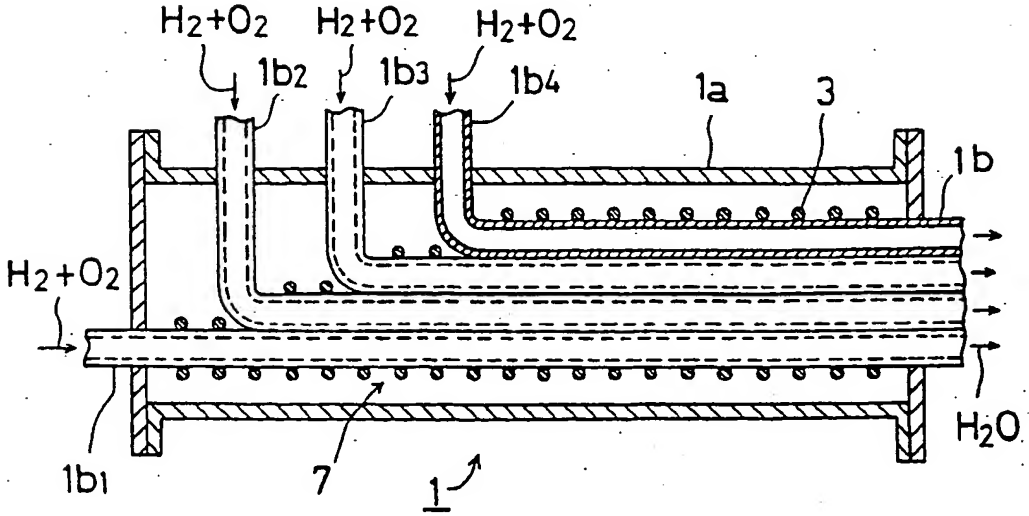


FIG. 14

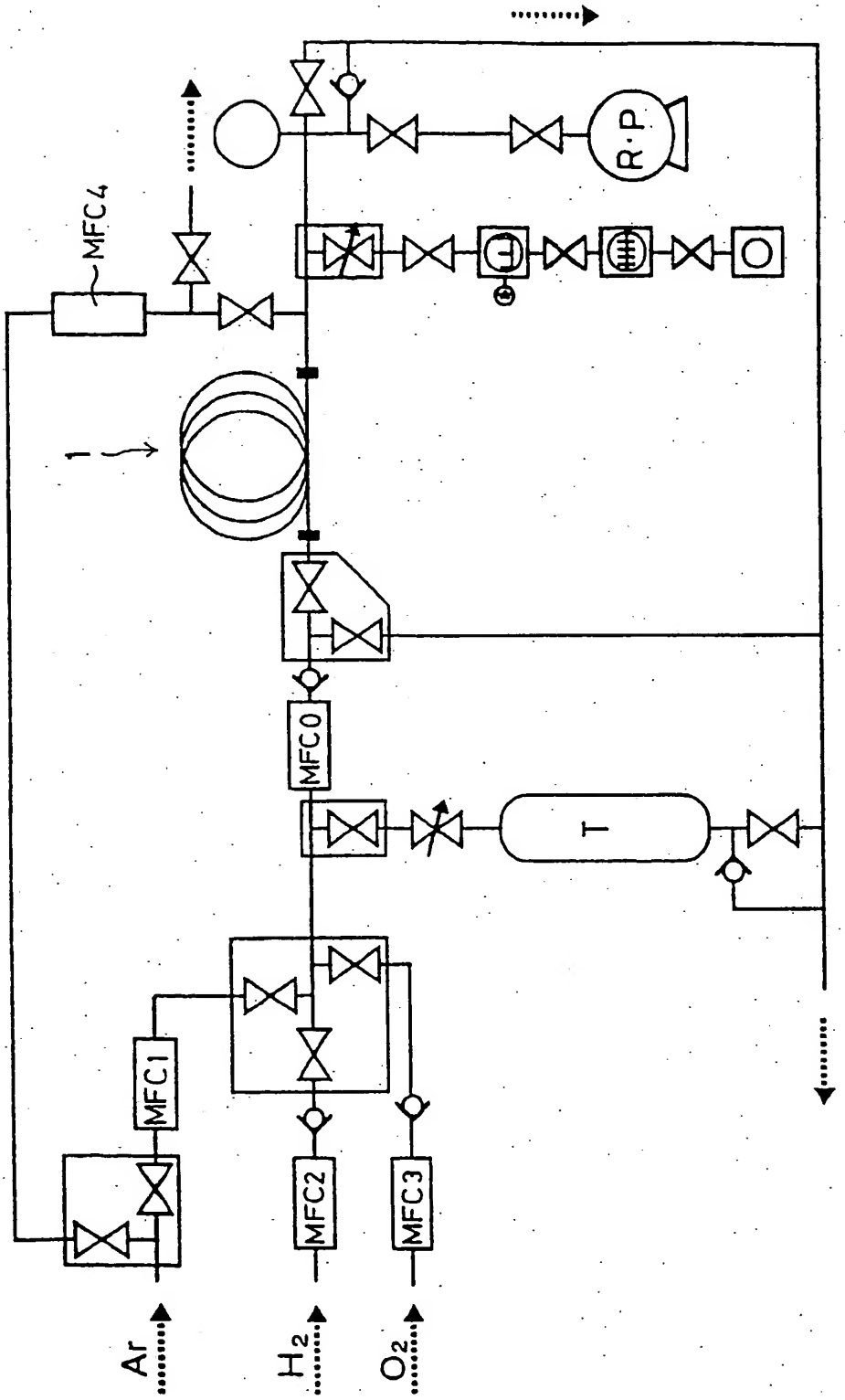


FIG. 17

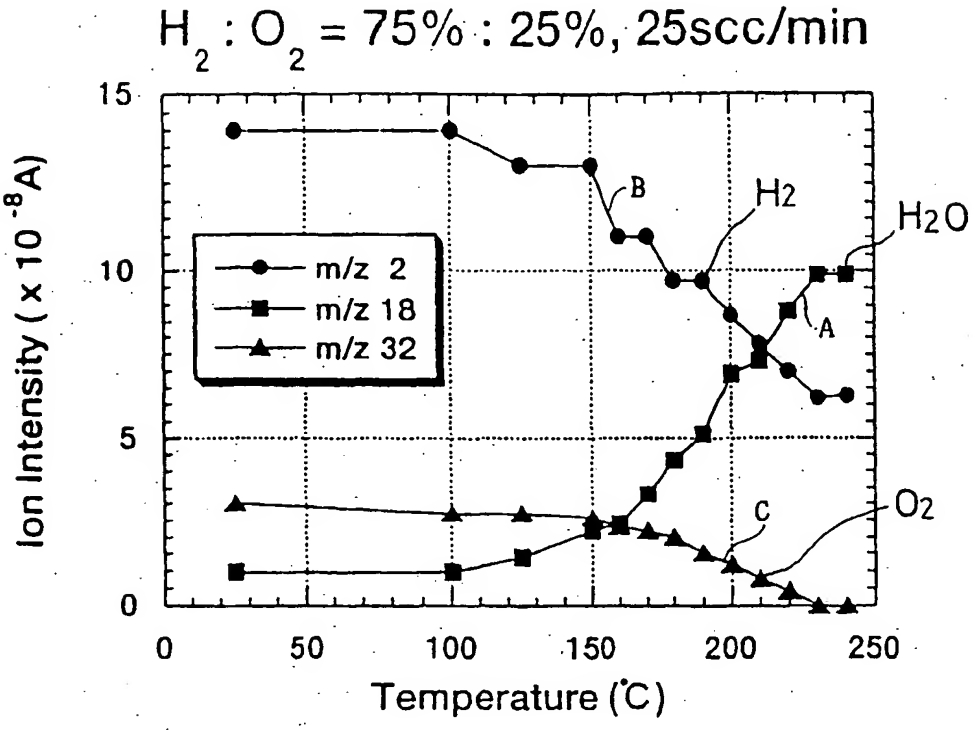

H2 : O2 = 75% : 25%, 25scc/min
Ion Intensity (x 10 -8A)
Temperature (°C)
m/z 2
m/z 18
m/z 32
B
H2
H2O
A
C
O2
0
5
10
15
0
50
100
150
200
250

FIG. 18

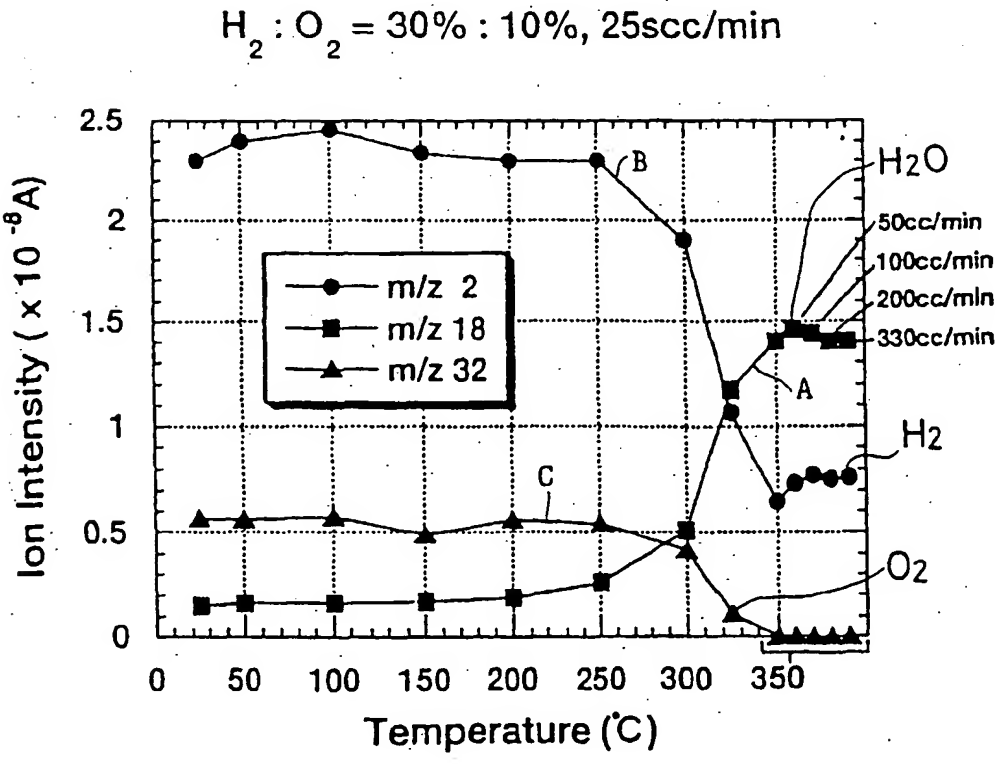

H2 : O2 = 30% : 10%, 25scc/min
Ion Intensity (x 10 -8A)
Temperature (°C)
m/z 2
m/z 18
m/z 32
B
H2O
50cc/min
100cc/min
200cc/min
330cc/min
A
H2
C
O2
0
0.5
1
1.5
2
2.5
0
50
100
150
200
250
300
350

FIG. 21

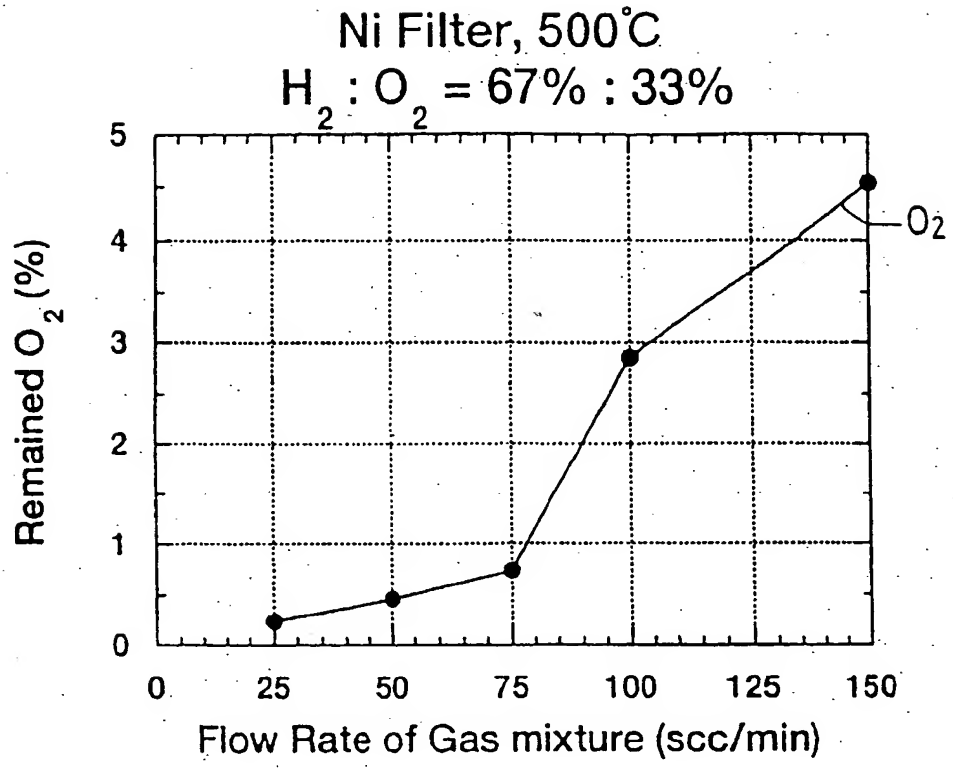

Ni Filter, 500°C
H2 : O2 = 67% : 33%
Remained O2 (%)
0
1
2
3
4
5
0
25
50
75
100
125
150
Flow Rate of Gas mixture (scc/min)
O2

FIG. 23

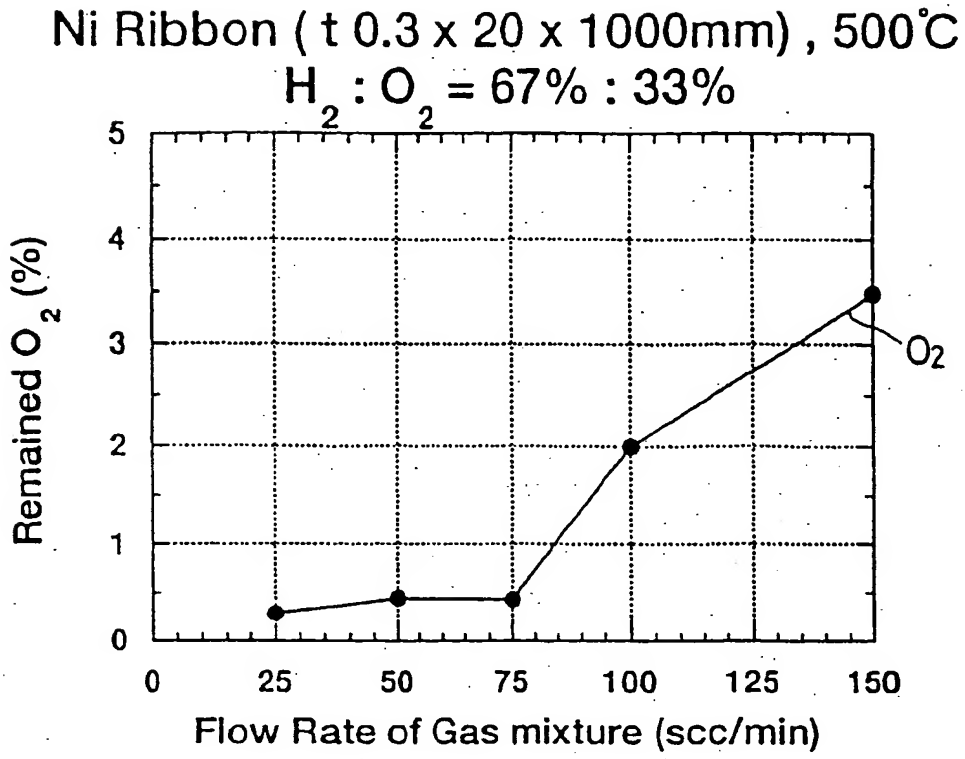

Ni Ribbon (t 0.3 x 20 x 1000mm) , 500℃
H2 : O2 = 67% : 33%
Remained O2 (%)
0
1
2
3
4
5
0
25
50
75
100
125
150
Flow Rate of Gas mixture (scc/min)
O2

FIG. 24

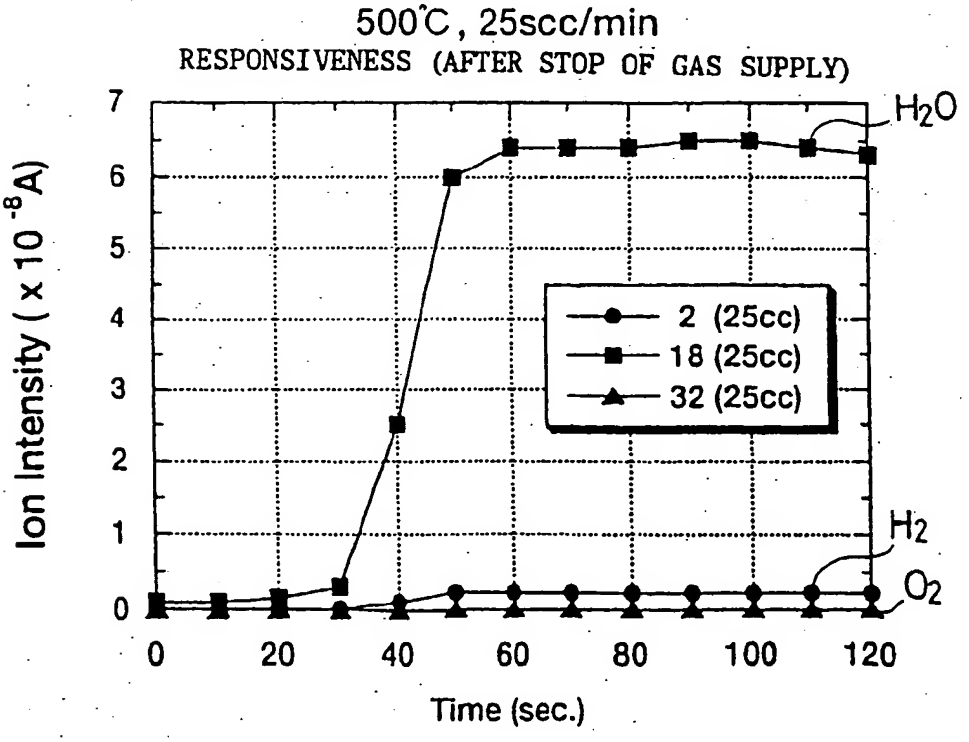

500℃, 25scc/min
RESPONSIVENESS (AFTER STOP OF GAS SUPPLY)
Ion Intensity (x 10 -8A)
0
1
2
3
4
5
6
7
0
20
40
60
80
100
120
Time (sec.)
2 (25cc)
18 (25cc)
32 (25cc)
H2O
H2
O2

FIG. 27

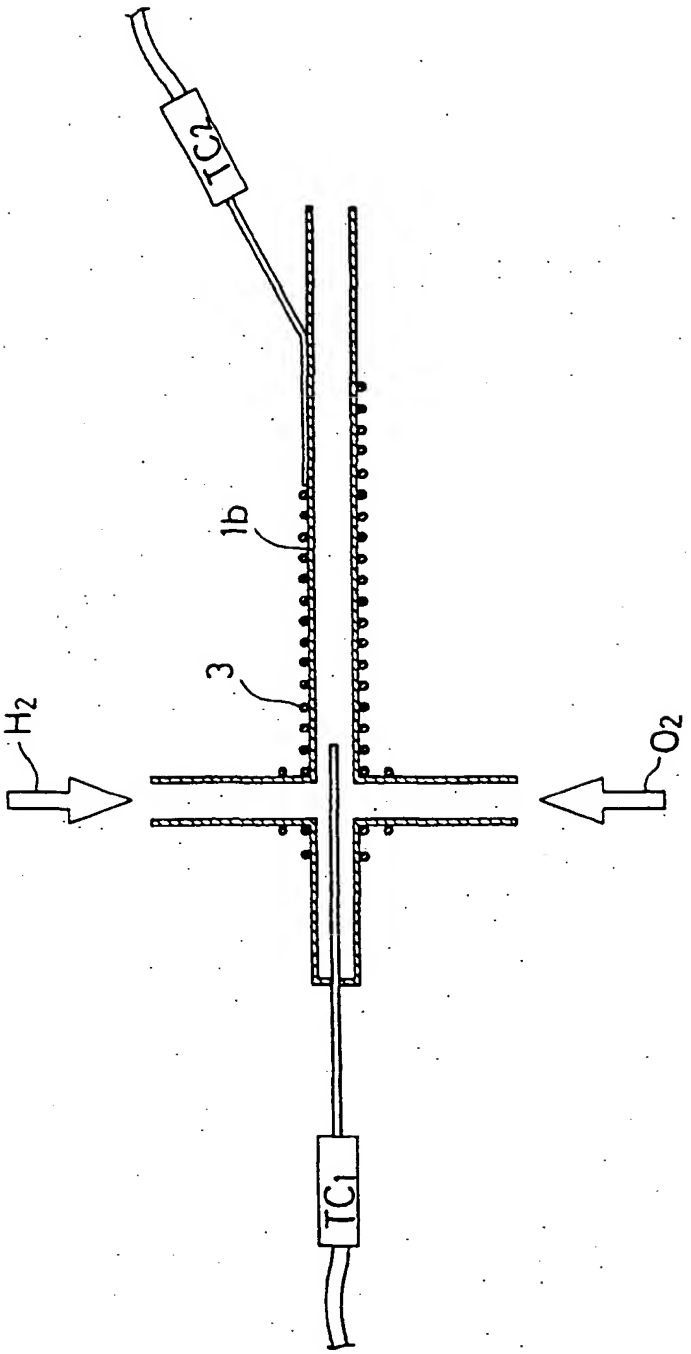


FIG. 29

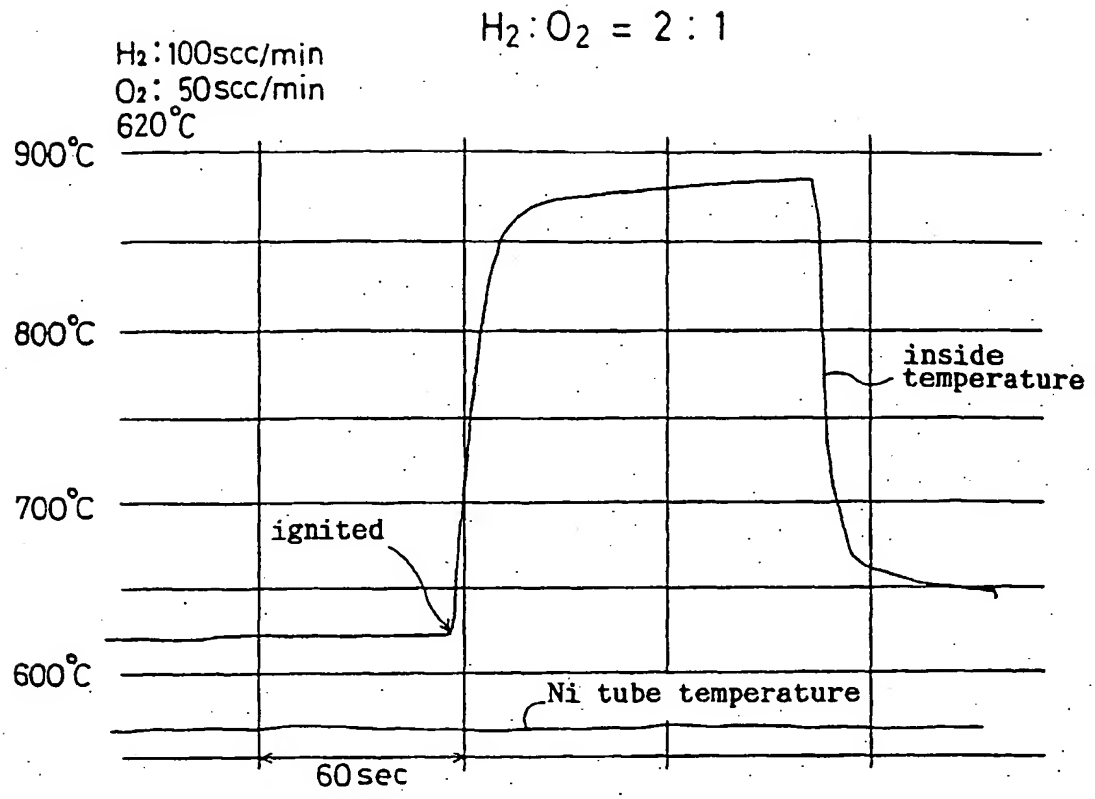

$H_2 : O_2 = 2 : 1$
H_2: 100scc/min
O_2: 50scc/min
620°C
900°C
800°C
700°C
600°C
inside temperature
ignited
Ni tube temperature
60sec

FIG. 30

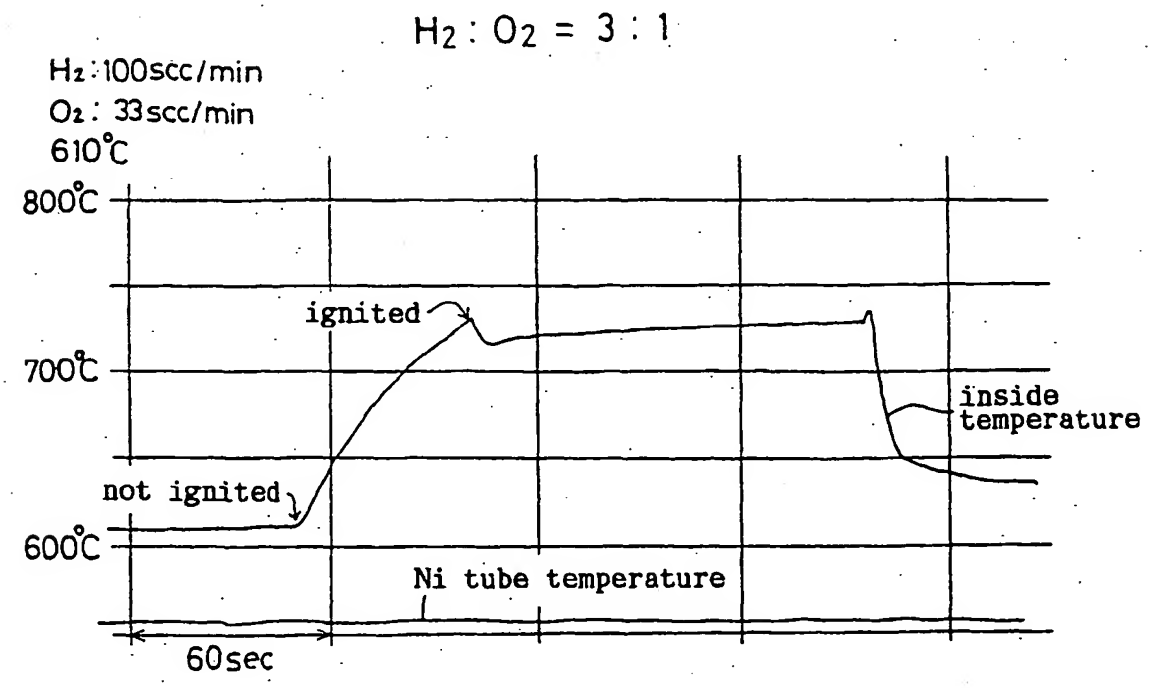

$H_2 : O_2 = 3 : 1$
H_2: 100scc/min
O_2: 33scc/min
610°C
800°C
700°C
600°C
ignited
not ignited
inside temperature
Ni tube temperature
60sec

FIG. 32

$H_2 : O_2 = 4 : 3$

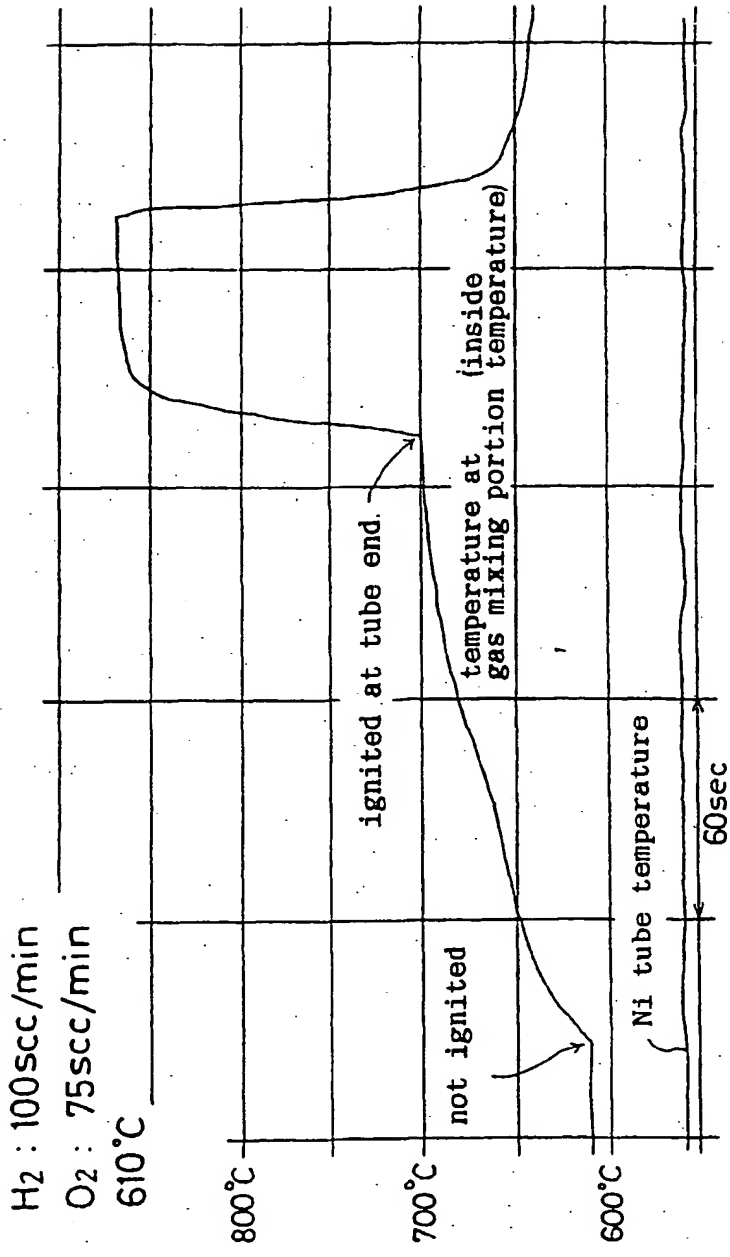


FIG. 35

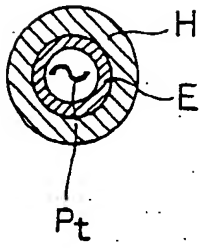


FIG. 36

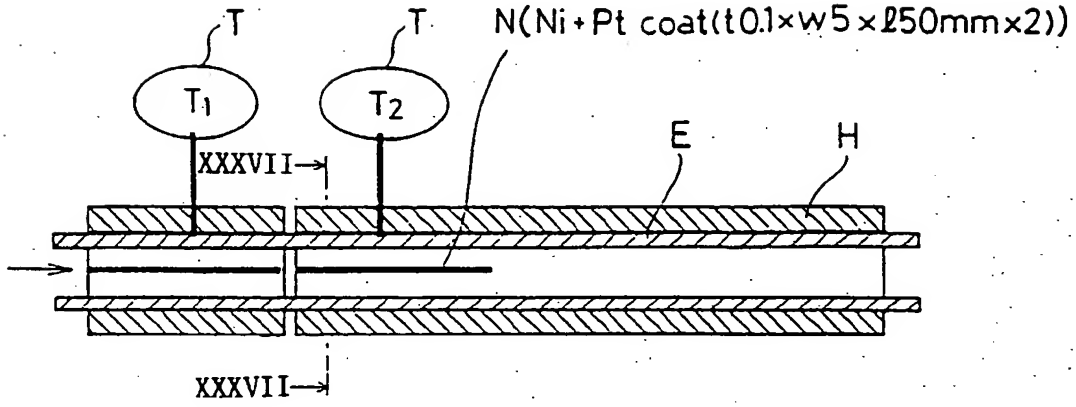


FIG. 37

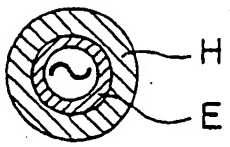
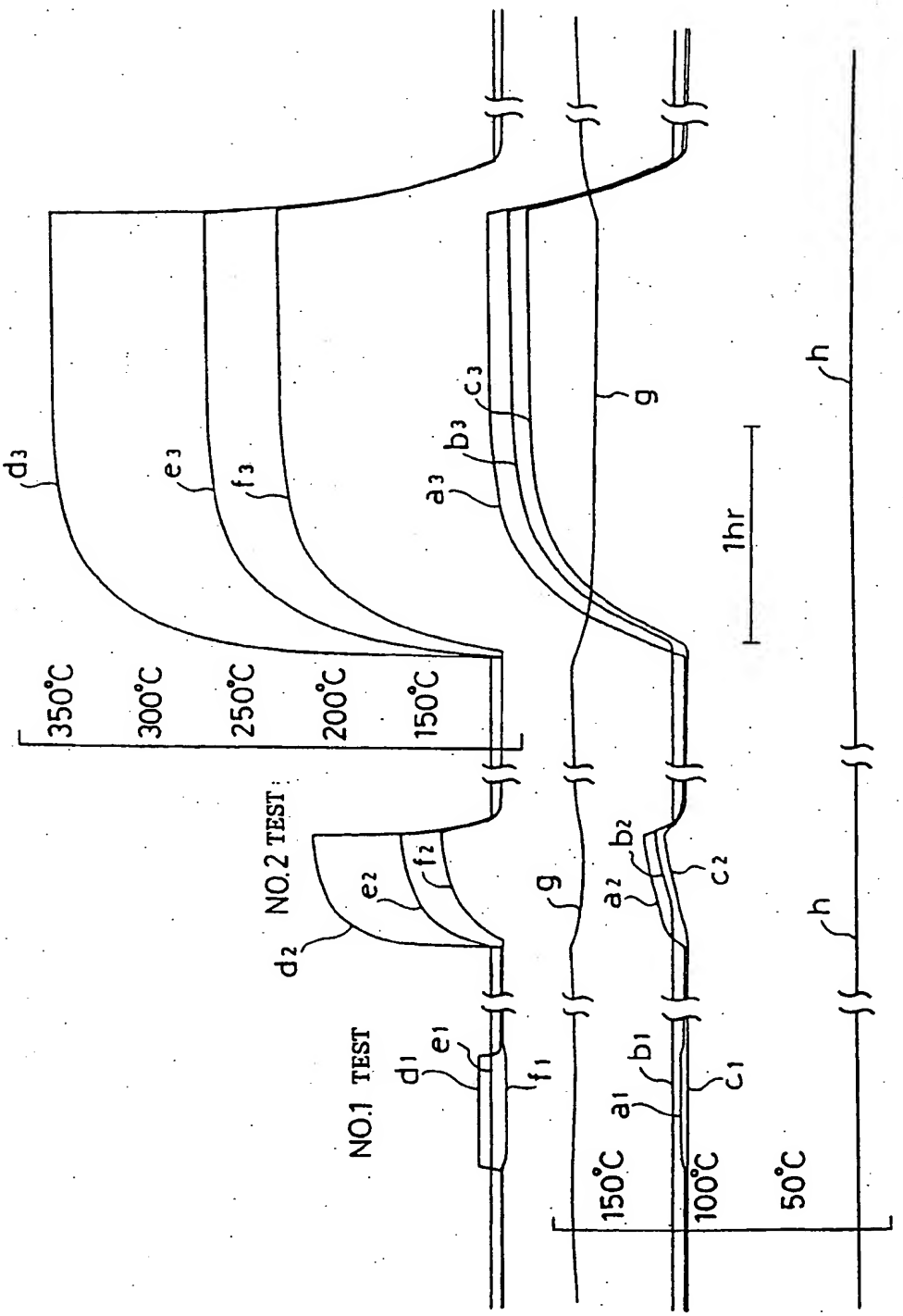


FIG. 40


NO.3 TEST
NO.2 TEST
NO.1 TEST
350°C
300°C
250°C
200°C
150°C
150°C
100°C
50°C
1hr
d3
e3
f3
a3
b3
c3
g
h
d2
e2
f2
a2
b2
c2
d1
e1
f1
a1
b1
c1

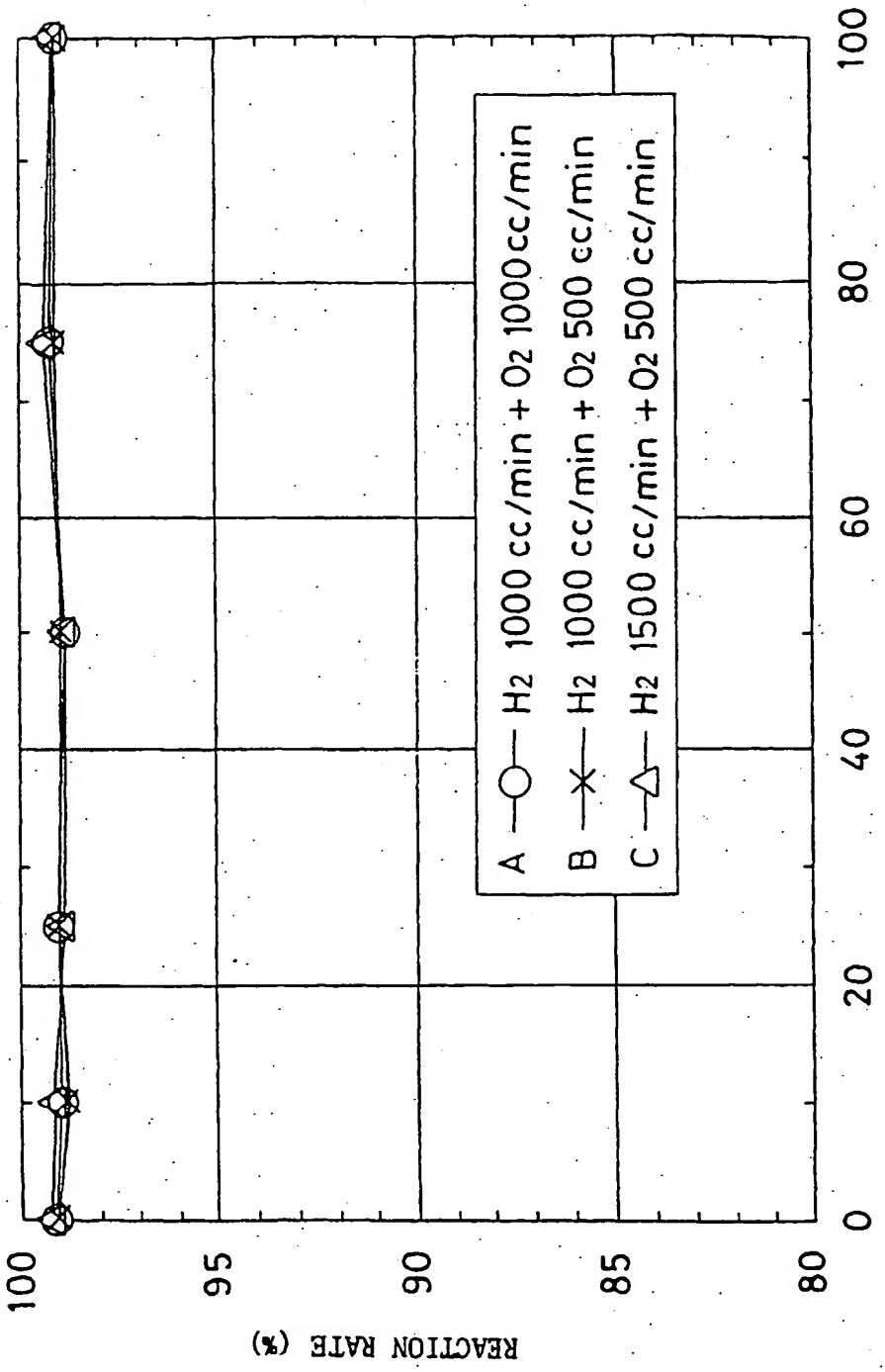

A — H2 1000 cc/min + O2 1000 cc/min
B — H2 1000 cc/min + O2 500 cc/min
C — H2 1500 cc/min + O2 500 cc/min
REACTION RATE (%)
100
95
90
85
80
0
20
40
60
80
100
TIME (h)

FIG. 42

FIG. 44

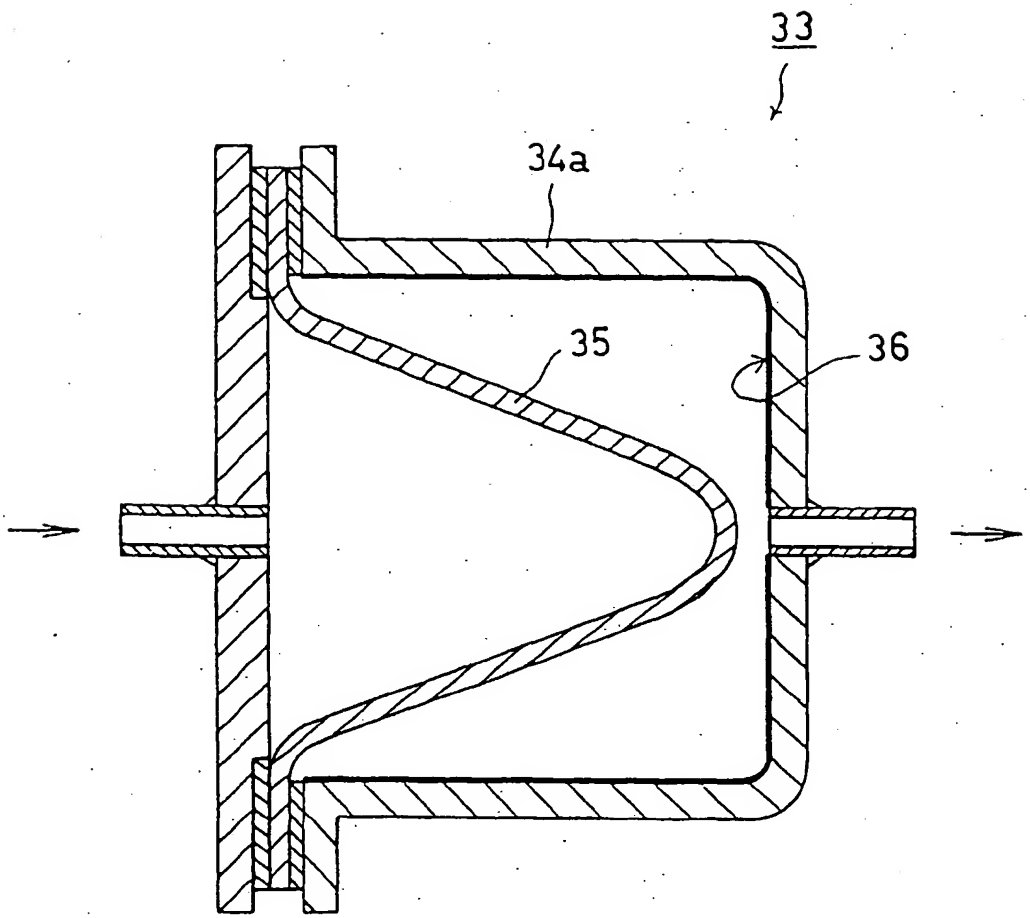


FIG. 46

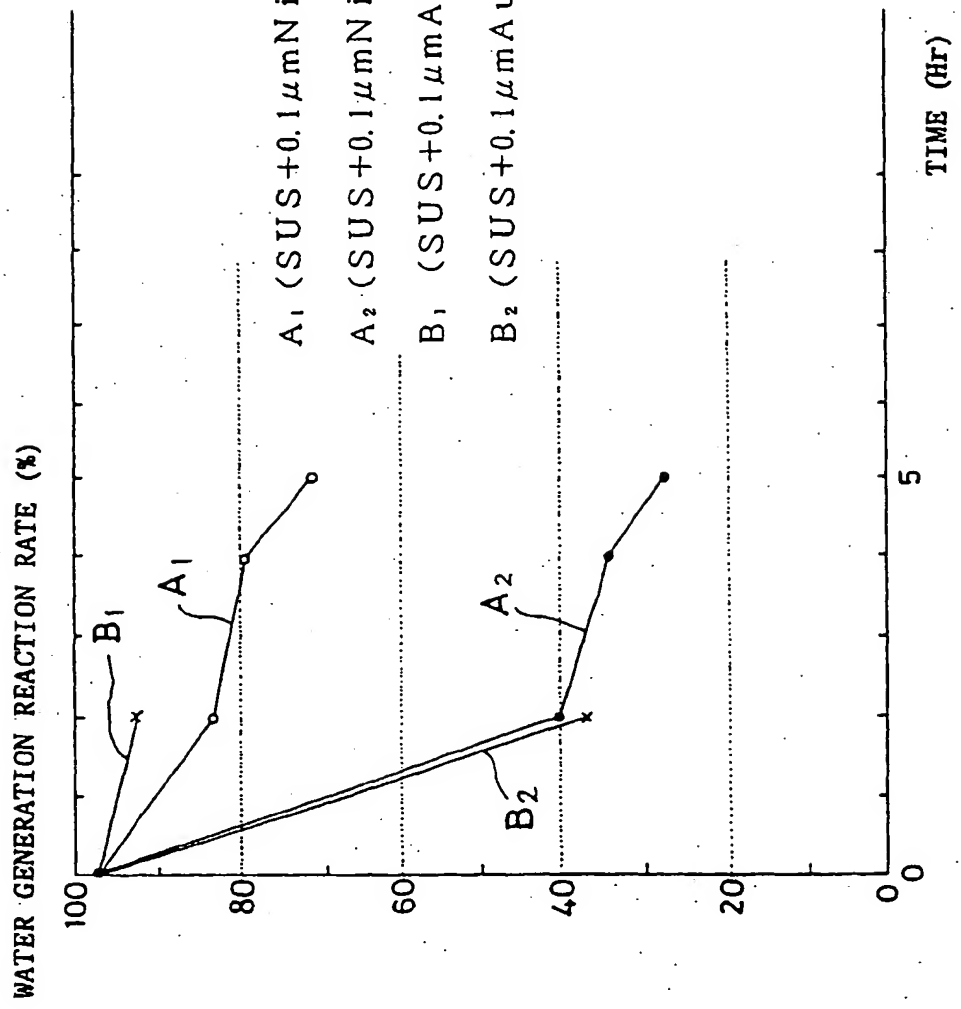

WATER GENERATION REACTION RATE (%)
100
80
60
40
20
0
0
5
TIME (Hr)
A1 (SUS+0.1μmNi+0.3μmPt) · 300℃
A2 (SUS+0.1μmNi+0.3μmPt) · 120℃
B1 (SUS+0.1μmAu+1μmPt) · 400℃
B2 (SUS+0.1μmAu+1μmPt) · 120℃
A1
A2
B1
B2

FIG. 48

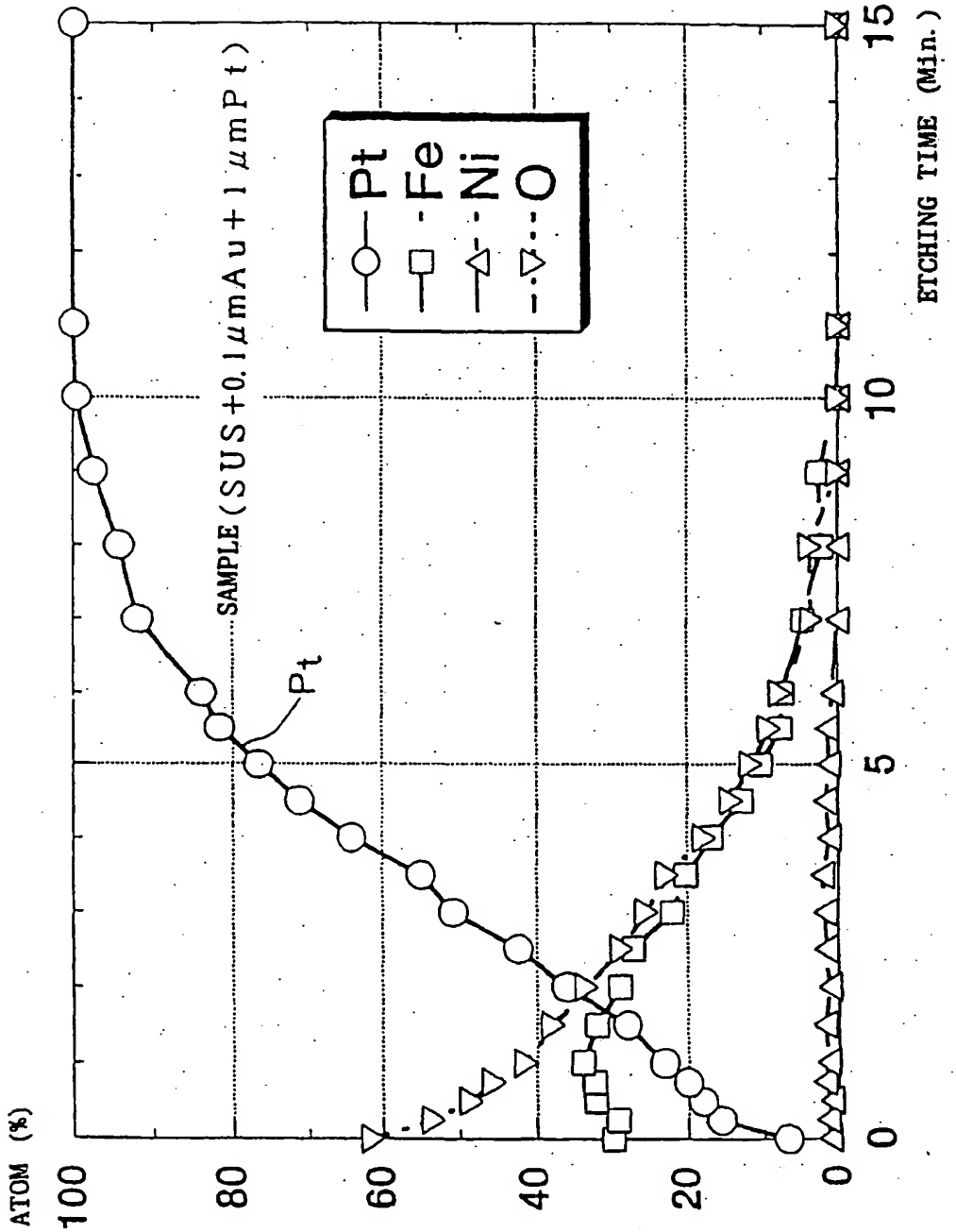

ATOM (%)
100
80
60
40
20
0
0
5
10
15
ETCHING TIME (Min.)
SAMPLE (SUS+0.1μmAu+1μmPt)
Pt
Fe
Ni
O
Pt

FIG. 50

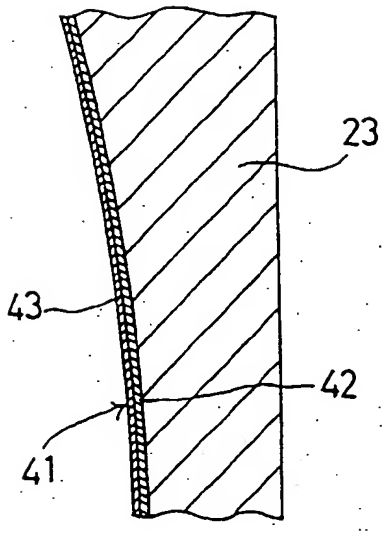


FIG. 52

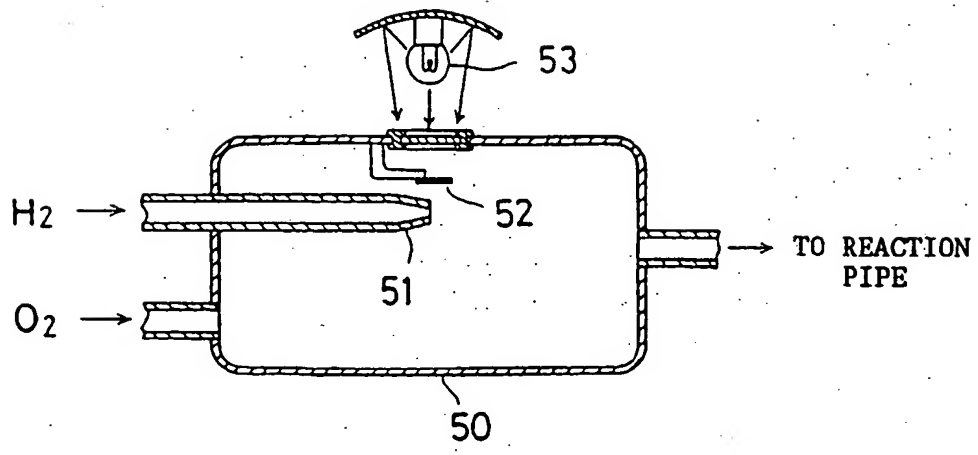
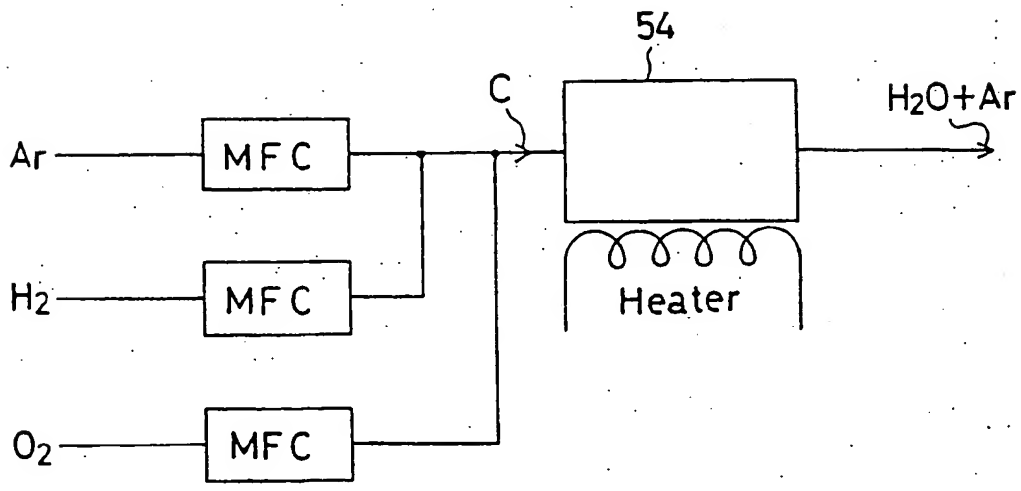

53
52
H_2
51
O_2
TO REACTION PIPE
50

FIG. 53


54
C
H_2O+Ar
Ar
MFC
H_2
MFC
O_2
MFC
Heater

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP97/00188

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	upper left column, line 6 (Family: none)	
X	JP, 63-85630, Y2 (Sumitomo Heavy Industries, Ltd.), December 18, 1992 (18. 12. 92), Claim; Fig. 1 (Family: none)	15-17, 19
A	JP, 04-54184, Y2 (Sumitomo Heavy Industries, Ltd.), December 18, 1992 (18. 12. 92), Claim; Fig. 1 (Family: none)	18, 20-33
A	JP, 55-41805, A (Tanaka Kikinzoku Kogyo K.K.), March 24, 1980 (24. 03. 80), Page 3, lower right column, line 4 to page 4, upper left column, line 6 (Family: none)	6-8, 12, 14